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Preparation, Structure, and Properties of Some Chromium Selenides. Crystal Growth with Selenium Vapor as a Novel Transport Agent

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Single crystals of three chromium selenides have been grown by chemical transport reaction. Monoclinic (M) and trigonal (T) forms of approximate composition Cr_2Se_3 were transported in the presence of selenium only, at pressures of 10 and 6 atm, respectively. Nonstoichiometric single crystals (T′) of $Cr_{0.68}Se$ were transported, without an excess of selenium, using iodine as a transport agent at a pressure of about 0.8 atm. The M phase has lattice constants $a = 6.227 \pm 0.001$ Å, $b = 3.582 \pm 0.001$ Å, $c = 11.528 \pm 0.002$ Å, and $\beta = 90.77 \pm 0.01°$ with space group I2/m. The T phase has $a = 12.509 \pm 0.002$ Å and $c = 34.765 \pm 0.005$ Å. The T′ phase is also trigonal, with $a = 3.612 \pm 0.001$ Å and $c = 5.775 \pm 0.002$ Å and probable space group P3m1. All phases are basically metal-vacancy NiAs structures. Vacant chromium sites are located in alternate metal layers along c. A mechanism for the transport of some transition metal selenides with selenium is proposed. A simplified chemical understanding of some transition metal chalcogenides, with Cr_xSe compounds, $1 > x > {}^5/_8$, as an example, is given in terms of n ionic cross-links of type $(1/v)Cr^{v+}$ between $[CrSe_2]_n^{n-}$ layers.

Introduction

Many transition metal chalcogenides have interesting magnetic, electrical, and optical properties, as extensively documented in the abstracts of the International Conference on Solid Compounds of Transition Elements at the Netherlands in 1967, and in Norway in 1969. Single crystals of numerous binary and ternary chalcogenides can be most readily grown by chemical transport reaction.[1] During such reaction there is always the possibility of contamination by the transport agent modifying the properties of the transported material. Contamination as high as 0.1% by weight has been reported for iodine as transport agent.[2] Schäfer, Wehmeier, and Trenkel[3] have recently shown numerous sulfides to be transported with sulfur as transport agent. Thus with sulfides, only components of a compound are necessary during transport reaction, hence avoiding contamination of the transported material.

In this paper the use of selenium as transport agent is reported. Single crystals of a monoclinic (M) and trigonal (T) phase of essentially stoichiometric Cr_2Se_3 are thereby grown for the first time. The technique is also used to grow single crystals of $TiSe_2$ and VSe_2. In addition, the growth of single crystals of another trigonal phase (T′) of composition $Cr_{0.68}Se$ is reported by transport with iodine. The growth of single crystals of phases M, T, and T′, followed by structural interpretation, has led to systemization of the Cr_xSe compounds. The chromium–selenium system Cr_xSe, $x < 1$, has been studied extensively in the past. Haraldsen and Mehmed[4] reported three phases of wide composition range (Table I). The α phase, for which $1 > x > 0.87$, was thought to have a hexagonal B8 structure. The β phase with $0.85 > x > 0.71$ was stated to be monoclinic, and the γ phase, with $0.70 > x > 0.68$, was assigned hexagonal symmetry. More recently, in a series of studies on powder samples Chevreton and coworkers[5-9] have identified phases of the following nominal compositions: Cr_7Se_8,[5] Cr_3Se_4,[5] Cr_2Se_3,[6,7] and $Cr_{0.68}Se$.[7] All these compounds were thought to be based on an NiAs-type structure (B8) with ordered chromium vacancies in alternate metal layers. Cr_7Se_8 and Cr_3Se_4 were stated to be monoclinic, Cr_2Se_3 was rhombohedral, and $Cr_{0.68}Se$ was either hexagonal B8 or trigonal (2c′ in their notation, T″ in ours—see Table II). Sleight and Bither[10] have recently grown single crystals of monoclinic Cr_5Se_8 at pressures in excess of 65 kbars.

Experimental Section

Commercially available starting materials were used: chromium metal powder, 325 mesh from United Mineral & Chemical Corp.; titanium metal sponge from Light & Co.; vanadium metal lumps and iodine from Gallard-Schlesinger; selenium granules from NPC Electronics. Manufacturers' nominal purity for each element is 99.9%.

Single crystals of Cr_2Se_3–M and –T, $TiSe_2$, and VSe_2 were prepared by chemical transport reaction with selenium; see Table III. Single crystals of Cr_2Se_3–T′ were transported with iodine. The experiments were carried out in transparent quartz ampoules having an internal diameter of 19 mm and a total length of about 120 mm. The starting materials were placed into the ampoules, evacuated to 10^{-2} Torr, sealed with a hydrogen torch, and heated in a horizontal resistance furnace with two independent heaters. Cr_2Se_3–M single crystals were prepared using chromium powder with an excess of selenium in a temperature gradient. Cr_2Se_3–T, $TiSe_2$, and VSe_2 single crystals were grown with an excess of selenium from previously prepared material in powder form. The selenium pressure inside the transport ampoule was generally between 3 and 10 atm.[11] In all

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(1) H. Schäfer, "Chemical Transport Reactions," Academic Press, New York, N. Y., 1964.

(2) H. Schäfer and H. Odenbach, *Z. Anorg. Allg. Chem.*, **346**, 127 (1966).

(3) H. Schäfer, F. H. Wehmeier, and M. Trenkel, *J. Less-Common Metals*, **16**, 290 (1968).

(4) H. Haraldsen and F. Mehmed, *Z. Anorg. Allg. Chem.*, **239**, 369 (1938).

(5) M. Chevreton and F. Bertaut, *C. R. Acad. Sci.*, **253**, 145 (1961).

(6) M. Chevreton, M. Murat, C. Eyraud, and E. F. Bertaut, *J. Phys. (Paris)*, **24**, 443 (1963).

(7) M. Chevreton and B. Dumont, *C. R. Acad. Sci., Ser. C*, **267**, 884 (1968).

(8) M. Chevreton, E. F. Bertaut, and S. Brunie, *Bull. Soc. Sci. Bretagne*, **39**, 77 (1964).

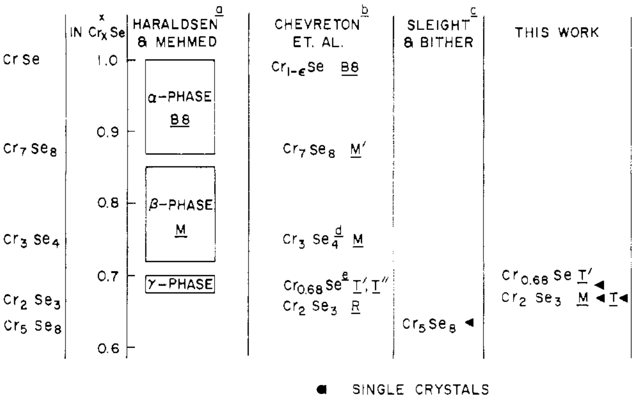
(9) M. Chevreton, *Bull. Soc. Fr. Mineral. Cristallogr.*, **90**, 592 (1967).

(10) A. W. Sleight and T. A. Bither, *Inorg. Chem.*, **8**, 566 (1969).

(11) Calculated assuming that only Se_2 molecules are present and that all excess selenium is in the vapor state. The true pressure in the ampoule is lower than this because of the presence of higher molecular species in the vapor and also the possible presence of liquid selenium.

TABLE I

Cr_xSe PHASES



[a] Reference 4. [b] References 5–9. [c] Reference 10. [d] Reference 9 states this phase to be continuous with $0.71 > x > 0.81$ on slow cooling and $0.64 > x > 0.83$ on quenching. [e] Reference 7 states the T″ phase has $0.68 \leqslant x \leqslant 0.69$.

TABLE II

Cr_xSe CRYSTAL DATA

Nominal formula	Structure type	Space group	*a*, Å	*b*, Å	*c*, Å	β, deg	*V*, Å³	*V*/Se, Å³	Ref
CrSe	B8	$P6_3/mmc$	3.71		6.03		71.9	35.94	*a*
Cr_7Se_8	M′	$F2/m$[f]	12.67	7.37	11.98	90.95	1119	34.97	*b*
Cr_3Se_4	M	$I2/m$[f]	6.32	3.62	11.77	91.47	269.2	33.65	*b*
$Cr_{0.68}Se$	T″	$P\bar{3}1c$	6.28		11.64		397.5	33.13	*c*
	T′	$P3m1$	3.612		5.775		65.24	32.62	*d*
Cr_2Se_3	M	$I2/m$[f]	6.227	3.582	11.528	90.77	257.1	32.14	*d*
	T	$P3$ (?)	12.509		34.765		4712	32.72	*d*
Cr_5Se_8	M″	$F2/m$[f]	12.353	7.148	11.462	91.06	1012	31.63	*e*

[a] F. K. Lotgering and E. W. Garter, *J. Phys. Chem. Solids*, **3**, 238 (1957). [b] Reference 5. [c] Reference 7. [d] This work. [e] Reference 10. [f] Unconventional setting allows easier comparison.

TABLE III

TYPICAL TRANSPORT CONDITIONS AND RESULTS

Entry no.	Starting material	Ampoule vol, ml	Se excess		Iodine wt, mg	Temp gradient, °C	Transport time, days	Residue X-ray pattern	Yield, mg	Transported material	
			Wt, mg	Se_2 pressure,[a] atm						Analysis	X-Ray pattern
1	$TiSe_2$[b] 700 mg	30	200	3.8	0	880→790	4	$TiSe_2$	350	$TiSe_{1.95}$[c]	$TiSe_2$
2	VSe_2[b] 610 mg	32	200	3.6	0	870→780	4	VSe_2	330	$VSe_{1.98}$[c]	VSe_2
3	Cr 1040 mg Se 2370 mg	34	520	10	0	1023→926	18	Cr_2Se_3–T	1200	$Cr_{0.65}Se$[c] $Cr_{0.67}Se$[d]	Cr_2Se_3–M
4	Cr_2Se_3[b]	6	317	35	0	1017–1017[e]	5	Cr_2Se_3–T	. . .	. . .	. . .
5	Cr_2Se_3[b]	4.5	643	95	0	1006–1006[e]	6	Cr_2Se_3–M	. . .	. . .	. . .
6	Cr_2Se_3[b]	40	340	6	0	1102→1031	18	Cr_2Se_3–T	370	$Cr_{0.66}Se$[c]	Cr_2Se_3–T
7	$Cr_{0.69}Se$[b]	32	0	0[f]	60	1012→922	20	$Cr_{0.68}Se$–T′	500	$Cr_{0.68}Se$[c]	$Cr_{0.68}Se$–T′

[a] See ref 11. [b] Prepared powders. [c] Combustion method. [d] X-Ray fluorescence. [e] Zero gradient maintained. [f] No excess was introduced. Some selenium is produced by the reaction of Cr_2Se_3 and I_2.

cases chemical transport took place from the hotter to the cooler part of the ampoule, with temperature differences as given in Table III. Two annealing experiments were carried out, at selenium pressures of 35 and 95 atm,[11] respectively, to investigate the stability of Cr_2Se_3–M. At the end of each experiment the ampoules were removed from the furnace and rapidly quenched to room temperature. The gas phase in all cases was condensed in the middle of the ampoule to avoid contamination of the transported crystals or the residue. In every case crystals grew at the cooler end of the ampoule.

Compositions were determined by combustion in air. The titanium and chromium oxides were subsequently heated at 900° for 4 hr; vanadium oxide was heated for 0.5 hr just above its melting point. The weight of metal was calculated from the oxide and the difference was assumed to be selenium. Typically, 75 mg of material was used for analysis, consisting of two or three crystals. The process was repeated at least once for each case. An X-ray spectrochemical analysis was also made for Cr_2Se_3–M.

Differential thermal analysis (dta) measurements were made with a Du Pont 900 dta machine at a heating rate of 20°/min. Aluminum oxide was used as a reference material. The selenides were enclosed in small quartz ampoules sealed under vacuum. Absorption spectra were examined using Perkin-Elmer spectrophotometers, Models 21 (2.5–5 μ) and 421 (5–30 μ).

Transport conditions and analytical results for some typical experiments are given in Table III. X-Ray powder photographs of all samples were taken on an Incentive Research and Development AB XDC 700 Guinier camera with Cu $K\alpha_1$ (λ 1.540562 Å) radiation, calibrated with quartz (a = 4.91347, c = 5.40513 Å). Lattice constants were obtained by least squares using a modification of Mueller and Heaton's program. Integrated intensities were measured on a Jarrel-Ash recording microdensitometer. Precession photographs of the chromium selenides were taken with Mo Kα radiation.

Crystal Growth and Proposed Structures

Cr_2Se_3–M, Cr_2Se_3–T, VSe_2, and $TiSe_2$ transported in the presence of an excess of selenium. No transport was observed without this excess.

VSe_2 and $TiSe_2$.—Thin platelets of vanadium selenide crystals, with a black metallic luster, were grown to 2 mm in maximum dimensions. The titanium selenide crystals were copper-colored thin plates also with a metallic luster, up to 10 mm in diameter. Growth conditions are shown in Table III. $TiSe_2$ crystals give less than 1% transmission in the 2.5–30-μ range. The compounds were identified by chemical analysis of the transition metal and by X-ray diffraction. Dta on $TiSe_2$ to 1100° and on VSe_2 to 900° showed no evidence of phase transition or of fusion. X-Ray photographs made from samples before and after the dta gave the same patterns.

Cr_2Se_3–M.—Under the conditions shown in Table III, entry 3, single crystals of the Cr_2Se_3–M phase were transported. Analysis by the combustion method gave a metal to chalcogenide ratio of 0.653 ± 0.005, whereas spectrochemical analysis gave 0.67 ± 0.01. The crystals, of essentially stoichiometric Cr_2Se_3, are lamellar hexagonal plates of lustrous metallic appearance, approximately 6 mm across the plate and 1 mm thick. No transmission was observed in the 2.5–30-μ range.

Precession and Laue photographs showed the crystals to be strongly pseudohexagonal, but with fundamental monoclinic symmetry. The unit-cell dimensions obtained from a Guiner powder photograph are a = 6.227 ± 0.001, b = 3.582 ± 0.001, c = 11.528 ± 0.002 Å, and β = 90.77 ± 0.01°. The indexed powder pattern data are given in Table IV. Reflections are systematically absent for $h + k + l = 2n$ in the powder pattern and on single-crystal photographs indicating the lattice to be body centered with space group I2/m (C_{2h}^3), I2(C_2^1), or Im (C_s^1). The centrosymmetric space group I2/m is assumed. This unconventional setting is retained for ease of comparison with the NiAs structure. The alternative C-centered cell with a' = 13.101, b' = 3.582, c' = 11.528 Å, and β = 151.62° may be obtained from the body-centered cell by the transformation $101/0\bar{1}0/00\bar{1}$. The observed density, measured pycnometrically, is 5.8 ± 0.1 g cm^{-3}. The calculated value is 5.84 g cm^{-3} for $Z = {}^8/_3$ formula weights of Cr_2Se_3, *i.e.*, $Cr_{5^1/_3}Se_8$, per unit cell.

TABLE IV

Cr_2Se_3–M X-RAY POWDER PATTERN

h	k	l	d_{obsd}, Å	d_{calcd}, Å	I_{obsd}
0	0	2	5.769	5.762	17
0	0	4	2.882	2.881	27
$\bar{2}$	0	2	2.755	2.754	43
$\bar{1}$	1	2	2.743	2.740	100
1	1	2	2.726	2.725	79
2	0	2		2.723	
$\bar{2}$	0	4	2.128	2.129	11
$\bar{1}$	1	4	2.119	2.119	40
1	1	4	2.104	2.100	21
3	1	0	1.795	1.795	68
0	2	0	1.790	1.790	26
$\bar{2}$	0	6	1.644	1.644	6
2	1	5	1.637	1.637	3
$\bar{1}$	1	6		1.638	
2	0	6	1.624	1.625	3
$\bar{3}$	1	4	1.531	1.532	3
0	2	4	1.521	1.521	3
3	1	4	1.515	1.516	2
$\bar{4}$	0	2	1.508	1.508	5
$\bar{2}$	2	2	1.501	1.501	5
2	2	2	1.496	1.496	6
0	0	8	1.441	1.440	5
$\bar{4}$	0	4	1.377	1.377	3
$\bar{2}$	2	4	1.370	1.370	5
2	2	4		1.362	
4	0	4	1.362	1.362	3

NiAs-type superlattice reflections were observed on single-crystal photographs, leading to the proposal that chromium vacancies are present. The composition is hence reconciled with the observed density. The chromium sites lie on sheets parallel to (001). An ideal structure is proposed in which alternate sheets are completely filled, thus accounting for four chromium atoms per cell. The remaining $1^1/_3$ chromiums are placed in one pair of twofold sites, each site having an occupancy of $^2/_3$; the remaining pair of sites is always vacant; see Figure 1. The proposed ideal structural parameters are listed in Table V.

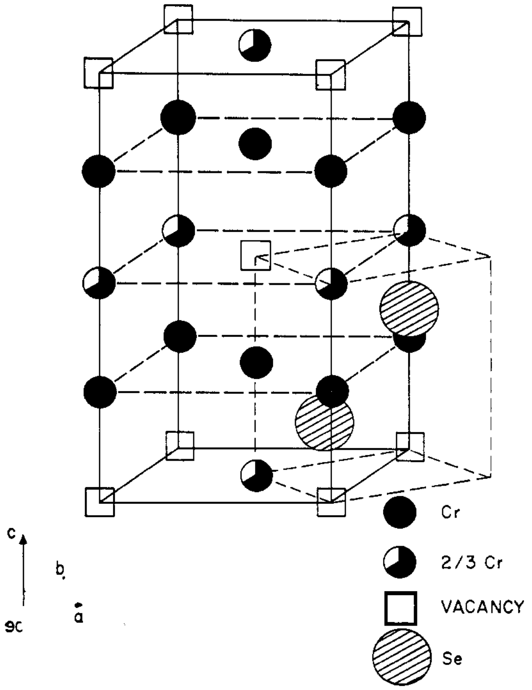


Figure 1.—Arrangement of metals and vacancies in Cr_2Se_3–M. The NiAs-type subcell is shown lightly dashed, with its selenium content. The chromium atoms are in sheets, alternately full.

TABLE V

Cr_2Se_3–M IDEAL ATOMIC PARAMETERS

Atoms	x	y	z
Se	$^2/_3$	0	$^3/_8$
Se	$^2/_3$	0	$^5/_8$
Cr	0	0	$^1/_4$
$^2/_3$ Cr	0	0	$^1/_2$
Vacancy	0	0	0

Cr_2Se_3–T.—A trigonal phase was transported and crystals were grown under the conditions shown in entry 6 of Table III. Analysis of this material, designated Cr_2Se_3–T, gave a Cr:Se ratio of 0.660 ± 0.005. X-Ray powder photographs of this phase appear identical with those of the residue of transport reactions (Table III, entry 3) yielding Cr_2Se_3–M as transport product.

The crystals of Cr_2Se_3–T were lustrous plates of metallic appearance, with hexagonal habit. The largest plates were 1 cm across. Very thin crystals appeared deep red in transmission. Crystals thicker than 0.1 mm gave less than 1% transmission between 2.5 and 30 μ. Single-crystal precession photographs indicated a prominent B8-type hexagonal subcell and a larger twinned rhombohedral subcell. All crystals examined appeared twinned. The true unit cell was trigonal with lattice parameters $a = 12.509 \pm 0.002$ and $c = 34.765 \pm 0.005$ Å obtained from Guinier photographs. The powder pattern of this phase, given in Table VI, is indexed on the basis of a rhombohedral subcell with $a' = 0.5a_{\text{true}}$ and $c' = 0.5c_{\text{true}}$. This is the unit cell assigned to a rhombohedral phase of nominal composition Cr_2Se_3 by Chevreton and Dumont[7] and also to the apparently isostructural Cr_2S_3 by Jellinek.[12] The absence of single crystals of a genuine rhombohedral phase, the possibility of indexing the powder pattern of Cr_2Se_3–T on the smaller cell, and the similar intensities given by Jellinek for Cr_2S_3 make it possible that the $(3c')$ phase of Chevreton and Dumont[7] is identical with our Cr_2Se_3–T phase.

TABLE VI

Cr_2Se_3–T′ X-RAY POWDER PATTERN

h	k	l[a]	d_{obsd}, Å	d_{calcd}, Å	I_{obsd}
0	0	3	5.794	5.793	4
0	0	6	2.894	2.896	8
1	1	3	2.753	2.751	100
1	1	6	2.125	2.125	36
3	0	0	1.806	1.805	47
3	0	3	1.723	1.723	5
1	1	9	1.643	1.643	15
3	0	6	1.532	1.532	9
2	2	3	1.510	1.509	27
0	0	12	1.449	1.448	5
2	2	6	1.376	1.376	22

[a] Based on rhombohedral subcell indexed on the basis of hexagonal axes. The 101, 012, and 104 lines are also observed, but are too weak for measurement.

A structure is proposed for Cr_2Se_3–T that is closely related to the structure proposed[7] for the rhombohedral subcell. This subcell contains chromium vacancies in alternate metal layers along [001]. The ideal coordinates of this structure based on the a' and c' rhombohedral subcell assuming symmetry $R\bar{3}$ are given in Table VII. Intensities calculated with the coordinates given in Table VII show good agreement with observed values reported in Table VI. The true unit cell has eight times the volume of the rhombohedral subcell and contains 48 formula weights. It is likely that the increased repeat unit is a result of a slight but ordered deviation from the 2:3 stoichiometry.

TABLE VII

Cr_2Se_3–T IDEAL ATOMIC PARAMETERS FOR RHOMBOHEDRAL SUBCELL

Atom	x	y	z
Cr	0	0	0
Cr	0	0	$^1/_2$
Cr	0	0	$^1/_3$
Se	$^1/_3$	0	$^1/_4$

Cr_5Se_8.—Attempts to prepare single crystals of this phase by vapor transport in thick-walled small bore quartz ampoules (i.d. = 0.125 in., o.d. = 0.625 in.) with selenium at calculated pressures of up to 95 atm[11] always resulted in Cr_2Se_3–M. Single crystals of Cr_5Se_8 have recently been prepared at 65 kbars in an anvil press by Sleight and Bither.[10]

$Cr_{0.68}Se$–T′.—The available literature on chromium selenides contains relatively little information regarding the "hexagonal γ phase" of Haraldsen and Mehmed,[4] reported to have the composition range $Cr_{0.70}Se$–$Cr_{0.67}Se$. A recent publication by Chevreton and Dumont[7] includes within this range a trigonal phase (T″), a disordered B8 structure, and structures of an intermediate type. Single crystals of composition $Cr_{0.68}Se$ have now been prepared in this laboratory and are found to have a disordered B8 structure of the type previously suggested.

The conditions given in Table III, entry 7, gave a transport product with a Cr:Se ratio of (0.675 ± 0.005):1. This represents the lower limit of the composition range of the γ phase.[4] The view that this compound "$Cr_{0.68}Se$" is significantly more chromium rich than Cr_2Se_3 is generally held.[4,7] Our product, labeled $Cr_{0.68}Se$–T′, is assigned this stoichiometry after Chevreton and Dumont,[7] although it is in fact representative of Cr_xSe for $0.675 < x < 0.700$.[4] In our experiments the transport product always gave the same composition on combustion ($Cr_{0.675}Se$) and identical X-ray powder patterns.

Single-crystal precession photographs showed apparent hexagonal symmetry. No systematic absences were observed. The presence of the 001 line in the powder pattern implies that the true symmetry is trigonal. It was found the structure may be conveniently but not exclusively described in space group P3m1. Unit cell dimensions determined from Guinier photographs are $a = 3.612 \pm 0.001$ and $c = 5.775 \pm 0.002$ Å. The observed powder data, given in Table VIII, are essentially the same as for the γ phase.[4] The density, measured pycnometrically, is 6.0 ± 0.1 g cm^{-3}. An assumption of two $Cr_{0.68}Se$ formulas per cell results in a calculated density of 5.94 g cm^{-3}.

TABLE VIII

$Cr_{0.68}Se$–T′ X-RAY POWDER PATTERN

h	k	l	d_{obsd}, Å	d_{calcd}, Å	I_{obsd}
0	0	1	5.768	5.774	10
0	0	2	2.892	2.887	10
1	0	1	2.751	2.750	100
1	0	2	2.121	2.121	53
1	1	0	1.806	1.805	42
1	0	3	1.639	1.639	10
1	1	2	1.530	1.531	3
2	0	1	1.509	1.509	6
2	0	2	1.375	1.375	4

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(12) F. Jellinek, *Acta Crystallogr.*, **10**, 620 (1957).

The unit cell of $Cr_{0.68}Se$–T′ is essentially that of hexagonal CrSe; *i.e.*, it represents a unit cell in the NiAs structure. The composition and density indicate chromium vacancies. The reduction of symmetry to trigonal from the ideal hexagonal results in the chromium atoms at $z = 0$ and $^1/_2$ becoming crystallographically independent. The assumption that all vacancies occupy alternate chromium layers along c, as shown in Figure 2, gives good agreement with the observed intensities of the powder pattern measured from Guinier photographs—Table VIII. The ideal atomic positions, as described in space group P3m1, are listed in Table IX.

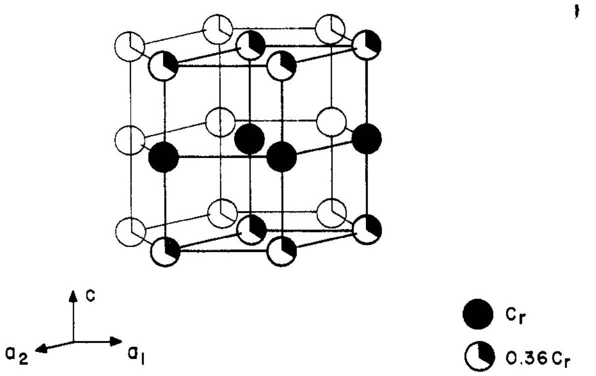

Figure 2.—Arrangement of fully and partially occupied metal sites in $Cr_{0.68}Se$–T′.

TABLE IX

$Cr_{0.68}Se$–T′ IDEAL ATOMIC POSITION COORDINATES

Atom	x	y	z
1Se	$^1/_3$	$^2/_3$	$^1/_4$
1Se	$^2/_3$	$^1/_3$	$^3/_4$
1Cr	0	0	$^1/_2$
0.36Cr	0	0	0

Discussion

In this section a mechanism for chemical transport of selenides by selenium is suggested. The structural aspects of the chromium–selenium system are summarized and an overall scheme is developed for a clearer insight into Cr_xSe materials and their properties.

The chemical transport mechanism of the selenides with an excess of selenium is not as yet understood. The possibility of sublimation is excluded by analogy with the case of transport of sulfides[3] with sulfur. In that system different transport directions are observed depending on the temperature. In addition, attempts to sublime the selenides without excess selenium resulted in no transport.

It is assumed that higher selenides are formed in the vapor by increasing the selenium pressure. One plausible model involves the formation of two or three n-membered selenium chains end-coordinated to the central metal atom, thus constituting two or three $(n + 1)$-membered rings with the metal, giving it a tetrahedral or octahedral coordination.

Attempts were also made to transport Cr_2Te_3 and $TiTe_2$ with tellurium in a temperature range between 1050 and 800°. No transport was observed. The approximate temperature–pressure[11] stability of the M, T, and T′ phases is shown in Figure 3. Generally, at lower temperatures and higher pressures the M phase is stable, while the T phase is formed at higher temperatures and moderate pressures. The T′ phase is stable at pressures lower than 0.1 atm. Sleight and Bither[10] prepared Cr_5Se_8–M″ in an anvil press at 65 kbars. Therefore it is likely that this compound is stable at pressures higher than those for M.

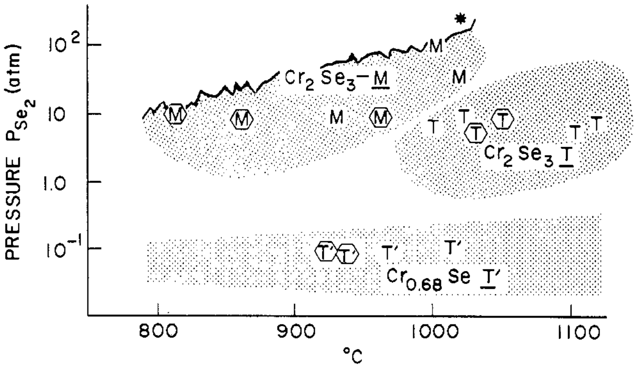

Figure 3.—Schematic diagram of the proposed selenium pressure *vs.* temperature stability ranges of some chromium selenides. Experimental points are indicated by the appropriate letters; those within a hexagon represent single crystal products. Upper portion of M phase (*) indicates the limit imposed by the maximum vapor pressure of selenium.

The preparative, analytical, and crystallographic results show that the temperature and selenium pressure applied during the preparation of the single crystals determines the selenium content of the phase. Thus the existence of three or more different compounds of approximate composition Cr_2Se_3 is due to small differences in the Cr:Se ratio. The three phases are not merely modifications of one and the same compound. The compounds are conveniently referred to as Cr_2Se_3–M, Cr_2Se_3–T, and $Cr_{0.68}Se$–T′, although none is strictly stoichiometric. However, the composition range of the monoclinic phase includes the stoichiometric (2:3) ratio.

All the Cr_xSe compounds in the range $1 > x \geq {^5/_8}$, as well as many other binary and some ternary chalcogenides of transition metals, possess NiAs-vacancy structures. The metal vacancy ordering in the Cr_xSe compounds leads to supercells of symmetry lower than the ideal hexagonal, as is summarized in Table II. The volume per selenium atom in the series decreases smoothly as the Cr:Se ratio decreases. The vacancies are distributed exclusively in alternate "vacancy sheets" along the pseudohexagonal c axis. A schematic view of a vacancy sheet in each of the Cr_xSe phases is shown in the sequence (a) to (g) of Figure 4. In $Cr_{0.68}Se$(T′), available chromium sites on alternate sheets have an evenly distributed partial occupancy (Figure 4(d)). Cr_2Se_3–T to a first approximation contains both completely filled and completely empty

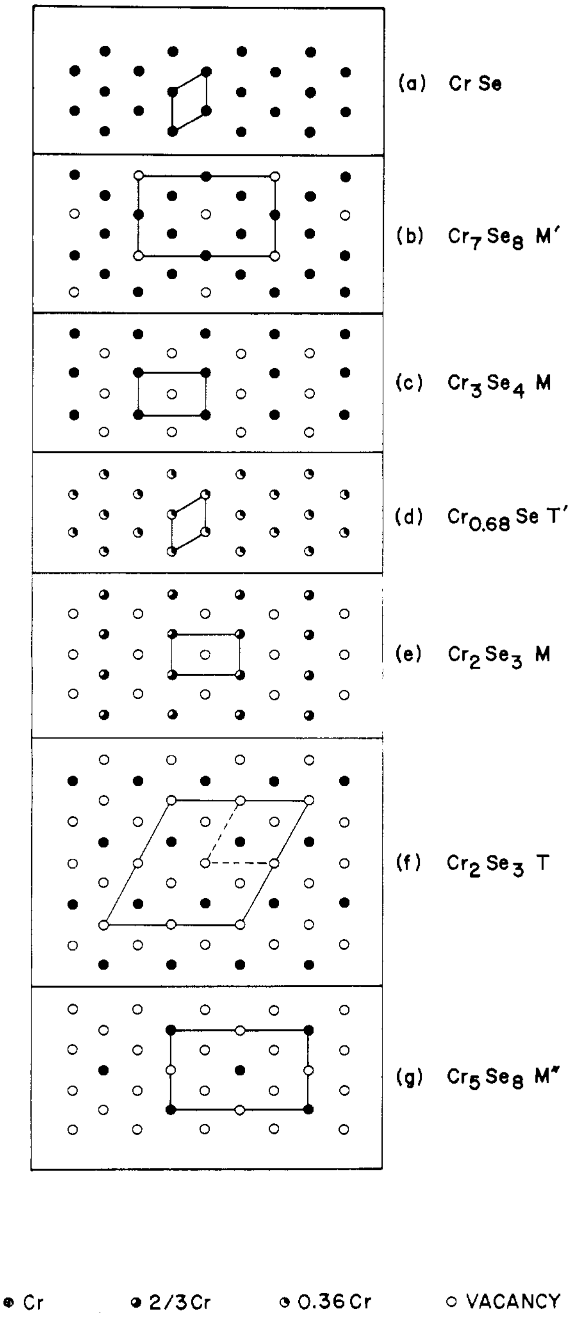

Figure 4.—Schematic view of a vacancy sheet in (a) CrSe, B8, (b) Cr_7Se_8–M′, (c) Cr_3Se_4–M, (d) $Cr_{0.68}Se$–T′, (e) Cr_2Se_3–M, (f) Cr_2Se_3–T, (g) Cr_5Se_8–M″. An outline of the unit cell is given in each case, as well as the subcell in (f) for T.

sites in the vacancy sheets (Figure 4(f)). Thus any transformation among these compounds, such as Cr_2Se_3–M → Cr_2Se_3–T, may be explained by a redistribution within the vacancy sheets.

The composition ranges in the Cr_xSe system, for $1 > x \geq {}^5/_8$, previously proposed on the basis of powder studies (Table I), are not inconsistent with the present single-crystal study. Deviations from nominal stoichiometry would affect only the number and arrangement of metal atoms in the vacancy sheet. Charge compensation may also be accomplished in terms of the vacancy sheet atoms. There is therefore no fundamental difference in this system between composition ranges and solid solution regions. The possibilities of changing the order in the vacancy sheet by heat treatment have not been investigated.

It is interesting to note that the arrangement of vacancies within all the monoclinic compounds, *i.e.*, Cr_7Se_8, Cr_3Se_4, Cr_2Se_3–M, and Cr_5Se_8, is quasicontinuous. Considering only a single sheet which is to become a vacancy sheet, removal of alternate atoms from alternate rows of the full CrSe arrangement (Figure 4(a)) gives Cr_7Se_8–M′, Figure 4(b). The array of atoms and vacancies (M) corresponding to Cr_3Se_4 may be derived by removing the remaining atoms from alternate rows (Figure 4(c)). Cr_2Se_3 corresponds simply to a reduction in occupancy of the remaining sites, whereas Cr_5Se_8 is obtained by removal of atoms from alternate sites in the M arrangement thereby resulting in the M″ array (Figure 4(g)), that is, a complement in two dimensions of the M′ repeat pattern.

The most persistent structural property of these compounds, however, is that the vacancy sheets always alternate with completely filled sheets. The whole system may hence be regarded on a different basis from that advanced previously. All the Cr_xSe compounds may be described in terms of n ionic cross-links of type $(1/v)Cr^{v+}$ between $[CrSe_2]_n^{n-}$ layers (*cf.* the $Cd(OH)_2$-type layers); each chromium is octahedrally coordinated and all octahedra within the layers share edges to form a continuous sheet in which the Se:Cr ratio is 2:1.

Essentially identical $[CrSe_2]_n^{n-}$ layers are proposed for all these compounds. Even CrSe can be visualized in these terms consistent with the suggestion of chromium deficiency in that compound.[6] The sequence of compounds in terms of the general formula $[CrSe_2]_n^{n-}(1/v)Cr^{v+}$ is presented in Table X. This sequence satisfactorily explains the structural features and metal to chalcogenide ratios found in this system. It represents stoichiometric "islands" in a virtually continuous system. Mechanisms of conductivity have been proposed previously in terms of charge hopping[13,14] or alternatively of direct overlap of orbitals.[14,15] If the first mechanism were correct, our model would imply metallic conductivity for Cr_xSe, $x \geq {}^7/_8$, and nonmetallic behavior for the stoichiometric compounds $x < {}^7/_8$. The direct-overlap mechanism is essentially independent of our model; thus we would expect the

TABLE X

Cr_xSe COMPOUNDS IN TERMS OF $[CrSe_2]_n^{n-}$ SHEETS AND $(1/v)Cr^{v+}$ CROSS-LINKS

Nominal formula	Representation in terms of $[CrSe_2]_n^{n-}(1/v)Cr^{v+}$	Representation in terms of A = Cr, B = $CrSe_2$
CrSe	$[CrSe_2]^- Cr^+$	AB
Cr_7Se_8	$[CrSe_2]^- {}^1/_4(Cr_2{}^+, Cr^{2+})$	A_3B_4
Cr_3Se_4	$[CrSe_2]^- {}^1/_2Cr^{2+}$	AB_2
Cr_2Se_3	$[CrSe_2]^- {}^1/_3Cr^{3+}$	AB_3
Cr_5Se_8	$[CrSe_2]^- {}^1/_4Cr^{4+}$	AB_4

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(13) E. F. Bertaut, A. Raoult, R. Alleonard, R. Pauthenet, M. Chevreton, and R. Jansen, *J. Physiol. (Paris)*, **25**, 582 (1964).

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conductivity behavior to be similar throughout the series. Conductivity measurements on this system[6, 10, 15–17] are inconsistent but favor the latter mechanism.

A new family of compounds may be proposed in which the link atom is replaced by a metal, A, of appropriate valency and size. Some materials of this type have already been prepared, *e.g.*, $NaCrSe_2$[18] and $FeCr_2Se_4$.[19] Examples of other possibilities are $GaCr_3Se_6$ or VCr_4Se_8. The substitution of other transition metals, B, for chromium, and chalcogens, Y, for selenium adds two further variables to this series, with the general formula $[BY_2]_n^{n-}\ (1/v)A^{v+}$.

The scheme of $Cd(OH)_2$-type layers with ionic cross-links may probably be extended to most NiAs-vacancy structures, in which the metal vacancies are located in alternate sheets. It also explains why many of the compounds with nominal metal to chalcogenide ratios of 1:1 are, in fact, always metal deficient.

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The Crystal Structure of a Dimeric Cobalt Compound Containing a Chloro Bridge

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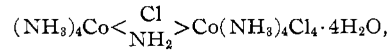
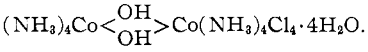
The compound μ-chloro-μ-amido-octaamminedicobalt tetrachloride tetrahydrate,  $(NH_3)_4Co{<}^{Cl}_{NH_2}{>}Co(NH_3)_4Cl_4\cdot 4H_2O$, forms triclinic crystals with cell dimensions $a = 7.812\ (1)$ Å, $b = 6.666\ (2)$ Å, $c = 20.577\ (4)$ Å, $\alpha = 107.02\ (2)°$, $\beta = 90.52\ (2)°$, $\gamma = 107.14\ (2)°$. The observed density is 1.77 (2) g cm^{-3}, and that calculated for two formula units in the cell is 1.771 (1) g cm^{-3}. All reflections with l odd are absent or extremely weak, indicating a pseudo structure with $c = 10.288$ Å. The pseudo structure has been solved and refined in space group $P\bar{1}$ by least-squares methods using 1018 reflections measured by counter diffractometry, to a final R index of 0.040. The two cobalt octahedra share an edge with the cobalt atoms 3.2 Å apart; the average cobalt–bridge chlorine distance is 2.325 (9) Å and the average cobalt–bridge nitrogen distance is 1.88 (2) Å. In this pseudo structure the bridging atoms are disordered, the cation lying on a center of symmetry. It is probable that the weak reflections with l odd are due to a partial ordering of the cation. The structure is approximately the same as that reported by Vannerberg and by Prout for  $(NH_3)_4Co{<}^{OH}_{OH}{>}Co(NH_3)_4Cl_4\cdot 4H_2O$.

Introduction

The mixture of cobalt compounds knows as Vortmann's sulfate[1] produces, upon treatment with nitric acid, two compounds, referred to by Werner as a red nitrate and a green nitrate.[2] The green compound has the formula $(NH_3)_4Co(O_2)(NH_2)Co(NH_3)_4(NO_3)_4$; its structure has been reported.[3] Werner named the red compound μ-sulfato-μ-amino-octaamminedicobalt nitrate; it can be transformed into many other dibridged compounds. We wish to report here the structure of one of these compounds; it is the first dicobalt species shown to contain a chloro bridge.

Experimental Section

Vortmann's sulfate was prepared and transformed to the nitrate according to Werner's directions.[2] The green nitrate was removed by extraction with water; the red nitrate which remained was mixed with a small amount of concentrated hydrochloric acid and left for several hours. The liquid was then sucked off and the solid residue was dissolved in warm, dilute hydrochloric acid; upon standing, a few large, red, triclinic crystals formed. Many of these crystals were obviously twinned, but some appeared to be single. They were all covered with a fine pink powder, and there was more of this powder in the beaker. Because only a few of the large crystals were formed, no chemical analyses were performed on the material. As will become clear, it is unfortunate that we do not have highly accurate chemical analyses, especially for nitrogen, of this compound, but none of our preparations ever gave crystals of only one variety, so no analyses were attempted.

Crystal data for the compound are collected in Table I; the tabulated cell dimensions and their errors were derived from a least-squares fit of 2θ values measured on the diffractometer for 21 reflections with 2θ between 72 and 146° and including both the Fe $K\alpha_1$ and $K\alpha_2$ peaks for each reflection. The density was measured both by flotation and by displacement of ethanol.

After the structure determination had been completed, Dr. A. W. Chester sent us a compound formulated as a monobridged

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