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New Chromium Chalcogenides Prepared at High Pressure and the Crystal Growth of Chromium Sesquisulfide

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The new chromium chalcogenides Cr_5S_8, Cr_5Se_8, and $Cr_5S_{4.8}Se_{3.2}$ have been prepared at pressures of 65–89 kbars. These phases have higher chalcogen-to-chromium ratios than have previously been reported in these systems. It is shown that they are isostructural with the known V_5S_8 and V_5Se_8 compounds. Their magnetic and electrical properties are reported, as well as the electrical properties of rhombohedral Cr_2S_3, which has been obtained for the first time in single-crystal form.

Introduction

The chromium–sulfur system has been extensively investigated by Jellinek.[1] In his work the phases CrS, Cr_7S_8, Cr_5S_6, Cr_3S_4, and Cr_2S_3 (two forms) were identified and their structures were established. The effect of high pressure upon the magnetic properties of both Cr_5S_6 and Cr_2S_3 through disordering is discussed by Yuzuri and Nakamura.[2] In the chromium–selenium system, the phases CrSe, Cr_7Se_8, Cr_3Se_4, and Cr_2Se_3 have been reported in detail.[3–5] The largest number of phases have been reported in the chromium–tellurium system and comprise CrTe, Cr_7Te_8, Cr_5Te_6, Cr_3Te_4, Cr_2Te_3, and Cr_5Te_8.[6–8]

The purpose of this work was to investigate the preparation of new chromium chalcogenides having high chalcogen-to-chromium ratios by using excess chalcogen at high reaction pressures. Phases of stoichiometry Cr_5X_8 (X = S and/or Se) were obtained, and their structures, as well as electrical and magnetic properties, were determined. In addition, single crystals of the known rhombohedral form of Cr_2S_3 were prepared, and their properties are reported.

Experimental Section

Preparation of Cr_5X_8 Compounds.—Reactions were carried out under pressure in a tetrahedral anvil press of National Bureau of Standards design[9] using a cylindrical boron nitride crucible surrounded by a graphite-sleeve resistance heater inserted in a pyrophyllite tetrahedron. The calibration points used to establish the pressure developed were the transitions Bi(I) → Bi(II) (25.37 ± 0.02 kbars), Bi(II) → Bi(III) (26.96 ± 0.18 kbars), Tl(II) → Tl(III) (36.69 ± 0.11 kbars), and Ba(II) → Ba(III) (59.0 ± 1.0 kbars). All compressions were made on the assembly at room temperature and the charge was then heated to the desired temperature which was measured with a Pt-Rh thermocouple, uncorrected for pressure effects. The thermocouple was adjacent to the center of the graphite heater.

High-purity reactants (>99.99% pure) were ground together and pelleted prior to reaction. Depending upon reactant densities, pellets weighed approximately 0.1–0.8 g.

The chromium sulfide phase was obtained in the form of black microcrystals when a mixture of Cr_2S_3–(1.0–1.5)S was pressured to 89 kbars and heated for 2 hr at 1200° followed by a quench to room temperature. The product was extracted overnight with CS_2 to remove unreacted S.

The chromium selenide and mixed-anion chromium sulfide selenide phases were prepared from a mixture of the elements of composition Cr–2Se or Cr–S–Se that was pressured to 65 kbars and heated for 2 hr at 1200° followed by a 4-hr cool to 400° and a quench to room temperature. Silvery, rod-shaped crystals formed at the sample ends in each case, and unreacted chalcogen was transported to the sample center. Crystals from the end regions only were used for characterization.

Preparation of Cr_2S_3 Single Crystals.—A mixture of 0.260 g of Cr and 0.641 g of S (Cr–4S) sealed in evacuated, heavy-walled silica tubing (8-mm o.d. × 8-cm length) was heated at 1350° under an external argon pressure of 3 kbars for 2 hr. The silica tubing flowed so as to transmit this pressure to the reactants. Following extraction with CS_2 to remove excess S, black platelets of Cr_2S_3 up to about 1 mm in length were isolated.

Chemical Composition.—The compositions of the new chromium sulfide and selenide phases were determined by thermogravimetry. Reaction in an oxygen atmosphere at a temperature up to about 1000° gave Cr_2O_3. With the sulfide and selenide binaries, the compositions $CrS_{1.62}$ and $CrSe_{1.60}$, *i.e.*, Cr_5X_8, were indicated. Assuming this ratio of chromium to chalcogen, a mixed sulfide–selenide $CrS_{0.96}Se_{0.64}$, *i.e.*, $Cr_5S_{4.8}Se_{3.2}$, was indicated. This ratio of S to Se was in good agreement with that calculated from the X-ray unit cell dimensions obtained on this phase as compared to those of the end members Cr_5S_8 and Cr_5Se_8. This use of Vegard's rule indicated the composition $Cr_5S_{4.9}Se_{3.1}$.

Electrical and Magnetic Measurements.—Except for Cr_5S_8, which was obtained only in powder form, electrical resistivity was measured on reasonably well-shaped single crystals using a standard four-probe technique. Activation energy of resistivity, E_a, is defined by the relation $\rho = \rho_0 e^{E_a/kT}$. A Faraday balance

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was used to measure magnetic properties in fields up to 8000 Oe. Both resistivity and susceptibility measurements were made to a lower temperature of 4.2°K.

X-Ray Data.—Single-crystal precession photographs were taken of Cr_5Se_8 and $Cr_5S_{4.8}Se_{3.2}$. Single crystals of Cr_5S_8 were not available. X-Ray powder photographs were taken at 25° using a Debye–Scherrer camera of radius 114.6 mm and Cr radiation ($\lambda(K\alpha)$ 2.2909 Å) and a Hägg–Guinier camera using strictly monochromatic Cu $K\alpha_1$ radition and a KCl internal standard (a = 6.2931 Å). The cell dimensions were refined by least squares. The observed intensities were determined qualitatively with a densitometer (David Mann film reader, Model No. 1222), and the calculated intensities were obtained by use of a program written by Parthe.[10] Absorption was ignored.

Results

Structural Studies.—Single-crystal photographs of Cr_5Se_8 and $Cr_5S_{4.8}Se_{3.2}$ showed strong hexagonal pseudosymmetry, but the true symmetry was monoclinic. A C-centered (space group C2, Cm, or C2/m) cell was indicated, but the single-crystal photographs could also be interpreted on the basis of a twinned, face-centered monoclinic cell of the same size or another C-centered cell of half the volume. It was decided to use the nonconventional face-centered monoclinic cell because of its more direct relationship to the hexagonal pseudocell. The assumed twinning is such that the crystals of the composite twin are related to each other by the sixfold axis of the hexagonal pseudocell. Such twinning is not uncommon in pseudohexagonal systems.

The powder patterns of the three phases Cr_5S_8, $Cr_5S_{4.8}Se_{3.2}$, and Cr_5Se_8 showed line splitting such that hexagonal indexing was impossible. These patterns were all successfully indexed on the basis of the monoclinic cell parameters indicated by the single-crystal photographs. All lines could be assigned indices in which h, k, and l were either all odd or all even, thus tending to confirm that the larger monoclinic cell was actually face-centered rather than C-centered. Unit cell dimensions for the three phases as refined by least squares from the powder data are given in Table I. For the conventional C-centered cell, a and b remain unchanged; however, the values for c' and β' of this smaller cell are also given in Table I. The volume for the C-centered cell is, of course, exactly half that of the face-centered cell.

TABLE I

UNIT CELL DIMENSIONS[a]

Parameter	Cr_5S_8	$Cr_5S_{4.8}Se_{3.2}$	Cr_5Se_8
a, Å	11.783 ± 0.010	11.981 ± 0.005	12.353 ± 0.004
b, Å	6.786 ± 0.006	6.931 ± 0.002	7.148 ± 0.004
c, Å	11.063 ± 0.008	11.245 ± 0.010	11.462 ± 0.003
β, deg	90.82 ± 0.02	90.11 ± 0.05	91.06 ± 0.01
a/b[b]	1.736	1.729	1.728
V, Å^3	844.5 ± 0.9	933.8 ± 0.9	1011.9 ± 0.5
c', Å	8.023 ± 0.006	8.208 ± 0.008	8.348 ± 0.002
β', deg	136.42 ± 0.02	136.76 ± 0.05	136.65 ± 0.01

[a] The data are for the nonconventional face-centered cell except for c' and β' which are for the conventional C-centered cell. [b] The "ideal" value of a/b is $\sqrt{3}$ or 1.732.

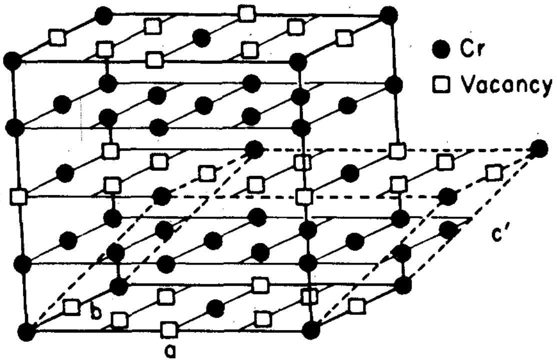

Figure 1.—Ideal structure of Cr_5X_8 phases. The chalcogenide atoms are omitted for clarity, but they may be regarded as essentially hexagonally close-packed as in the NiAs structure.

Since the cell dimensions, space group, and metal-to-chalcogen ratio for these three chromium chalcogenides are analogous to those of V_5S_8 and V_5Se_8, X-ray intensities were calculated assuming the ideal structure (Figure 1) proposed for V_5S_8 and V_5Se_8.[11] The space group is F2/m for the larger cell and C2/m for the smaller cell. The positions assumed for F2/m are 4 Cr_1 at 0, 0, 0; 8 Cr_2 at $^1/_4$, y, $^1/_4$ ($y = {}^1/_4$); 8 Cr_3 at x, 0, z ($x = {}^1/_2$, $z = {}^1/_4$); 8 X_1 at x, 0, z ($x = {}^1/_6$, $z = {}^1/_8$); 8 X_2 at x, 0, z ($x = {}^2/_3$, $z = {}^1/_8$); and 16 X_3 at x, y, z and $x, -y, z$ ($x = {}^5/_{12}$, $y = {}^1/_4$, $z = {}^1/_8$). Only positions for the asymmetric unit are given; the remaining positions for the cell can be derived from the center of symmetry and the face-centered operation.

The observed and calculated d values and intensities for Cr_5S_8 and Cr_5Se_8 are compared in Table II. All possible indices up to the cutoff are given, and the agreement is very good. The number of positional parameters, 10, was considered too great for a meaningful refinement of the powder X-ray data, and the crystals prepared to date are apparently twinned. Consequently, accurate descriptions of the Cr_5S_8 and Cr_5Se_8 structures cannot be given at this time. There is, however, little doubt but that they, and their solid solution, possess the structure which has been proposed for V_5S_8 and V_5Se_8. Since no refinement was undertaken and since the observed intensities are only qualitative, no R values have been calculated.

Electrical and Magnetic Properties.—The Cr_2S_3 in single-crystal form described herein had an X-ray powder pattern essentially identical with that of the rhombohedral Cr_2S_3 reported by Jellinek[1] and was observed to show semiconductor-type behavior. Room-temperature resistivity was 7 × 10^3 ohm-cm, and an activation energy of resistivity, E_a, of 0.05 eV was indicated in this temperature region. The Seebeck coefficient (α) at 46° was +1600 μV/deg. The Cr_2Se_3 phase is also reported[5] to be semiconducting at room temperature; *i.e.*, $\rho \simeq 1$ ohm-cm, $E_a = 0.025$ eV, and $\alpha = -190$ μV/deg.

Although single crystals of Cr_5S_8 were not available, the mixed-anion composition $Cr_5S_{4.8}Se_{3.2}$ had an activation energy of resistivity near room temperature com-

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Table II

X-Ray Powder Data for Cr_5Se_8 and Cr_5S_8

Cr_5Se_8					Cr_5S_8			
d calc	d obs	I/Io calc	I/Io obs	h k l	d calc	d obs	I/Io calc	I/Io obs
6.175	6.162	3	5	2 0 0	5.891	5.887	9	10
5.730	5.729	21	30	0 0 2	5.531	5.531	73	75
5.465	5.428	4	10	-1 1 1	5.208	5.170	14	30
5.423		4		1 1 1	5.177		14	
4.240	4.230	1	1	-2 0 2	4.061	-	4	-
4.162	4.158	1	1	2 0 2	4.004	-	4	-
3.574	-	.7	-	0 2 0	3.393	-	2	-
3.422	3.417	1	2	-3 1 1	3.261	3.244	4	10
3.391		1		3 1 1	3.238		4	
3.264	3.237	1	2	-1 1 3	3.134	3.116	4	10
3.237		1		1 1 3	3.114		3	
3.088	-	.2	-	4 0 0	2.945	2.942	19	40
3.093	-	.5	-	2 2 0	2.940		10	
3.033	-	.8	-	0 2 2	2.892	-	3	-
2.865	2.865	15	25	0 0 4	2.766	-	.02	-
2.739	2.732	51	85	-4 0 2	2.615	2.601	52	50
2.733		29		-2 2 2	2.604		3	
2.712	2.712	100	100	2 2 2	2.589	2.582	100	100
2.697	2.697	15	25	4 0 2	2.585		1	
2.618	2.626	.3	1	-2 0 4	2.517	2.511	1	5
2.628		.5		-3 1 3	2.515		2	
2.581	2.589	.3	1	2 0 4	2.490	2.481	1	5
2.588		.5		3 1 3	2.484		2	
2.336	2.291	.4	1	4 2 0	2.224	2.217	1	5
2.296		.3		-5 1 1	2.188	2.178	1	5
2.294		.3		-1 3 1	2.179		1	
2.291		.3		1 3 1	2.177		1	
2.280		.3		5 1 1	2.177		1	
2.235	-	.3	-	0 2 4	2.144	-	1	-
2.156	2.152	.3	1	-1 1 5	2.076	-	.9	-
2.174		.3		-4 2 2	2.071	-	.9	-
2.143		.3		1 1 5	2.066	-	.9	-
2.153		.3		4 2 2	2.056	-	.9	-
2.120	2.120	15	15	-4 0 4	2.031	2.031	22	30
2.112	2.112	30	30	-2 2 4	2.022	2.022	45	45
2.092	2.092	30	30	2 2 4	2.007	2.007	44	40
2.081	2.081	14	15	4 0 4	2.002	2.002	22	35
2.059	-	.1	-	6 0 0	1.964	-	.3	-
2.033	-	.2	-	-3 3 1	1.932	-	.7	-
2.026	-	.2	-	3 3 1	1.928	-	.7	-
2.008	-	.2	-	-5 1 3	1.917	1.906	.7	5
1.998	-	.2	-	-1 3 3	1.905		.7	
1.992	-	.2	-	1 3 3	1.901		.7	
1.977	-	.2	-	5 1 3	1.894		.7	
1.942	-	.2	-	-3 1 5	1.865		.6	
1.949	-	.1	-	-6 0 2	1.859	1.849	.3	5
1.914	-	.2	-	3 1 5	1.844		.6	
1.910	-	.8	-	0 0 6	1.844		3	
1.926	-	.1	-	6 0 2	1.842		.3	
1.834	-	.1	-	-2 0 6	1.767	1.744	.3	5
1.815	-	.1	-	2 0 6	1.752		.3	
1.823	-	.2	-	-4 2 4	1.742		.5	
1.822	-	.2	-	-3 3 3	1.736		.5	
1.808	-	.2	-	3 3 3	1.726		.5	
1.798	-	.2	-	4 2 4	1.724		.5	
1.784	1.784	41	65	6 2 0	1.700	1.699	22	70
1.787		20		0 4 0	1.697		44	

parable with those of the Cr_2X_3 compounds; *i.e.*, $\rho_{300°K} = 5 \times 10^{-3}$ ohm-cm and $E_a = 0.02$ eV. The resistivity of Cr_5Se_8 was 7×10^{-4} ohm-cm at room temperature and remained essentially unchanged down to 4.2°K.

Magnetic measurements in the form of inverse susceptibility *vs.* temperature curves are shown in Figure 2 for the Cr_5X_8 compounds, and the data are summarized in Table III. A Curie–Weiss dependence is observed for all three compounds from the high-temperature susceptibility data, and within experimental error essentially three unpaired spins per Cr atom are indicated in accord with the trivalent ion. Although no true Neel point is suggested for the Cr_5X_8 compounds from the data in Figure 2, some type of magnetic ordering is observed below room temperature. In both Cr_5S_8 and $Cr_5S_{4.8}Se_{3.2}$ this ordering is field independent, but in Cr_5Se_8 weak parasitic ferromagnetism is observed below 100°K.

Table III

Magnetic Properties of Cr_5X_8 Compounds[a]

Cr_5X_8	μ_{eff}, μ_B	θ, °K	$10^3 C_g$, emu °K/g Oe
Cr_5S_8	4.05	−688	19.69
$Cr_5S_{4.8}Se_{3.2}$	4.08	−510	15.63
Cr_5Se_8	3.74	−48	9.804

[a] Data are from the Curie–Weiss law [$\chi_g = (C_g/T - \Theta)$] as indicated in Figure 2. The effective moment for each chromium (μ_{eff}) is derived from C_g. The values are very similar to those generally observed for trivalent chromium; *e.g.*, see B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, 6, 126 (1964). The moments expected for a $Cr^{III}{}_4Cr^{IV}X_8$ situation would not necessarily be significantly different from the observed values.

Discussion

It is of interest to see whether the structural principles developed by Jellinek[1] for the lower chromium sulfides apply to Cr_5S_8 as well. The structure of Cr_5S_8 may be regarded as derived from the NiAs structure, as is the case for the other chromium sulfides. There are cation vacancies in every second layer along the

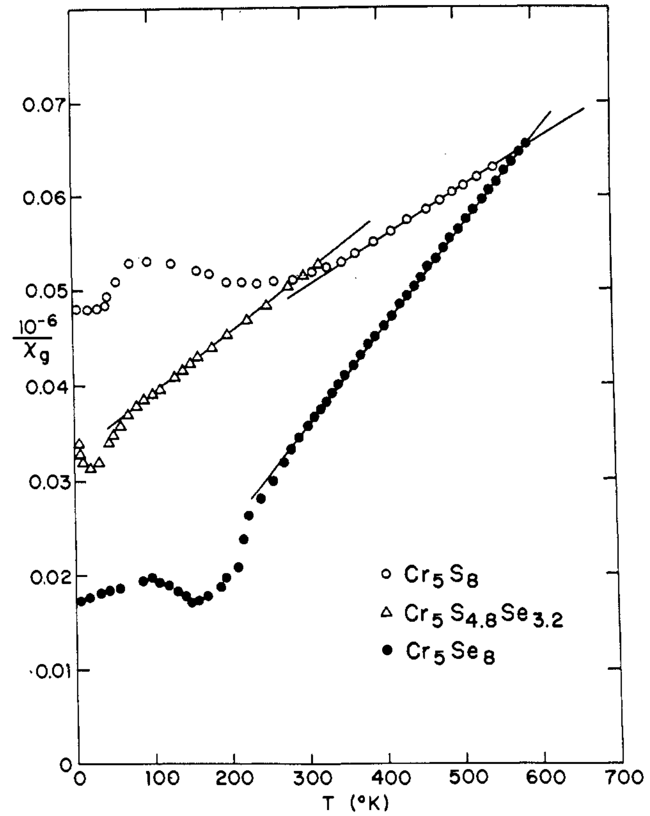

Figure 2.—Magnetic susceptibility of Cr_5X_8 phases: $1/\chi_g$ *vs.* *T*.

c axis, and these vacancies are ordered. Jellinek has pointed out that for structures of this type the only ordered compositions intermediate between CrX and CrX_2 (hypothetical) that may preserve trigonal symmetry are Cr_2X_3 and Cr_5X_6. It was thus expected that Cr_5X_8 phases of this work would not be hexagonal or trigonal if the cations were all ordered. It is interesting that although separately the ideal cation and anion lattices for ordered Cr_5X_8 and Cr_7Se_8 have hexagonal symmetry, their combination in this structure precludes the possibility of symmetry higher than monoclinic. This is true even if the hexagonal pseudocell shows no distortion.

The Cr_5X_8 formula may be rewritten as $Cr_4Cr'\square_3X_8$, where Cr′ is in the layer with the vacancies. The structures of $Cr_3Cr'\square_2S_6$ (trigonal Cr_2S_3) and $Cr_3Cr'_2\square S_6$ are essentially the same with only the Cr′ and vacancies being exchanged. The ordered structures of $Cr_4Cr'\square_3X_8$ and $Cr_4Cr'_3\square Se_8$ have the same relationship. Since the magnetic and electrical properties of these new Cr_5X_8 phases indicate that the d electrons of chromium are localized (with the possible exception of Cr_5Se_8), their formulas might be written as $Cr^{III}{}_4Cr^{IV}X_8$. From electrostatic considerations, it seems likely that the filled cation layers contain Cr^{III}, whereas the partially filled layers contain Cr^{IV}.

Although the electrical and magnetic data for Cr_5S_8 and $Cr_5S_{4.8}Se_{3.2}$ indicate localized electron behavior for chromium, the situation is less clear for Cr_5Se_8. The resistivity data indicate metallic or degenerate semiconducting behavior. The effective paramagnetic moment per chromium is lower in Cr_5Se_8 than in Cr_5S_8 and $Cr_5S_{4.8}Se_{3.2}$, and this may be a further indication that some electron delocalization is occurring. The resistivity of powder compacts of Cr_5Te_8 is reported[8] as low also indicating possible electron delocalization.

Recent work at this laboratory[12] has demonstrated that copper will readily attain a divalent state in sulfides with as little as 15 kbars of reaction pressure. On the other hand, we have now shown that a unique tetravalent state for chromium in a sulfide or selenide has not been achieved, even at reaction pressures up to 89 kbars. This difference in ease of oxidation may thus be taken as additional evidence that in the compounds $CuCr_2S_4$ and $CuCr_2Se_4$, the valence states $Cu^{II}Cr^{III}{}_2X_4$[13,14] are more likely than $Cu^{I}Cr^{III}Cr^{IV}X_4$ as originally proposed.[15]

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