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MULTIPLE ORDER IN SULFIDES AND SELENIDES

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Résumé. — On a découvert un nouveau type de structure cristalline (structures à ordre multiple) pour les composés hexagonaux $A_{1-p}Cr_2X_{4-p}$ ($A = Ba, Sr, Eu, Pb$; $X = S, Se$; $p \approx 0,29$). On peut considérer cette structure comme étant l'intercroissance de trois unités structurales ayant un plan de base hexagonal commun ($a \approx 21,5 \text{ \AA}$ pour $X = S$; $a \approx 22,5 \text{ \AA}$ pour $X = Se$), mais des axes c différents et incommensurables. Des octaédres CrX_6 aux arêtes et faces communes forment un édifice à trois dimensions de composition $Cr_{21}X_{36}$ avec $c_0 \approx 3,45 \text{ \AA}$ pour $X = S$; $c_0 \approx 3,63 \text{ \AA}$ pour $X = Se$. Cet édifice laisse subsister de larges canaux autour des axes d'ordre trois et six. Les canaux autour des axes d'ordre six contiennent une unité $A_6Cr_2X_6$ par distance répétitive c_6 ($c_6 \approx 5,7 \text{ \AA}$ pour $X = S$; $c_6 \approx 6,0 \text{ \AA}$ pour $X = Se$), les canaux autour des axes ternaires une unité A_3X par distance de répétition c_3 ($c_3 \approx 4,2 \text{ \AA}$ pour $X = S$; $c_3 \approx 4,6 \text{ \AA}$ pour $X = Se$). La composition des produits est déterminée par les rapports c_6/c_0 et c_3/c_0 . Les positions respectives des trois unités structurales dans la direction c sont reliées en $Ba_{1-p}Cr_2Se_{4-p}$ (qui constitue une surstructure commensurable avec $c = 5c_0 = 4c_3 = 3c_6$), mais virtuellement sans corrélation dans $Pb_{1-p}Cr_2S_{4-p}$. Dans les autres composés les positions des unités autour des axes d'ordre six et de l'édifice n'ont pas de corrélation (il en résulte des réflexions diffuses), mais les unités autour des axes ternaires sont liées à l'édifice et modulées en conséquence (il en résulte des réflexions et satellites fins). Les paramètres structuraux de $Eu_{1-p}Cr_2Se_{4-p}$ sont donnés.

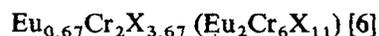
Abstract. — A novel type of crystal structure (structures with *multiple order*) has been found for the hexagonal compounds $A_{1-p}Cr_2X_{4-p}$ ($A = Ba, Sr, Eu, Pb$; $X = S, Se$; $p \approx 0.29$). The structure may be described as an intergrowth of three structural units which have a common hexagonal basal plane ($a \approx 21.5 \text{ \AA}$ for $X = S$; $a \approx 22.5 \text{ \AA}$ for $X = Se$), but different — and mutually incommensurate — c axes. CrX_6 octahedra sharing edges and faces form a three-dimensional framework of composition $Cr_{21}X_{36}$ with $c_0 \approx 3.45 \text{ \AA}$ for $X = S$; $c_0 \approx 3.63 \text{ \AA}$ for $X = Se$. This framework leaves wide channels around the sixfold and threefold axes. The channels about the sixfold axes contain a unit $A_6Cr_2X_6$ per repeat distance c_6 ($c_6 \approx 5.7 \text{ \AA}$ for $X = S$; $c_6 \approx 6.0 \text{ \AA}$ for $X = Se$), the channels about the threefold axes a unit A_3X per repeat distance c_3 ($c_3 \approx 4.2 \text{ \AA}$ for $X = S$; $c_3 \approx 4.6 \text{ \AA}$ for $X = Se$). The composition of the compounds is determined by the ratios c_6/c_0 and c_3/c_0 . The mutual positions of the three structural units in the c direction are related in $Ba_{1-p}Cr_2Se_{4-p}$ (which has a commensurate superstructure with $c = 5c_0 = 4c_3 = 3c_6$), but virtually uncorrelated in $Pb_{1-p}Cr_2S_{4-p}$; in the other compounds the positions of the units about the sixfold axes and the framework are not correlated (resulting in diffuse reflections), but the units about the threefold axes are correlated with the framework and modulated by it (resulting in sharp reflections and satellites). Structural parameters are given for $Eu_{1-p}Cr_2Se_{4-p}$.

Introduction. — In 1968 Omloo *et al.* [1] reported the synthesis and some properties of a series of compounds to which the general formula « ACr_2X_4 » was assigned, where A is a large divalent cation (Sr, Ba, Pb, Eu) and $X = S$ or Se . The compounds were found to be hexagonal with $a \approx 21.5 \text{ \AA}$; $c_0 \approx 3.45 \text{ \AA}$ for the sulfides and $a \approx 22.5 \text{ \AA}$; $c_0 \approx 3.63 \text{ \AA}$ for the selenides. In later studies the compounds formulated as $SnCr_2S_4$ [2], SrV_2X_4 , EuV_2X_4 [3] and $EuTi_2S_4$ [4] were found to possess the same type of structure.

While the vanadium compounds are metallic, the chromium compounds « ACr_2X_4 » were found to be semiconducting and ferrimagnetic, except for

« $BaCr_2S_4$ » which is antiferromagnetic [3]. The interesting magnetic properties of the chromium compounds, in particular those of « $EuCr_2X_4$ », have been the subject of several investigations. However, the discussion and interpretation of these properties was hampered by uncertainties about the correct chemical composition of the compounds and by the fact that their crystal structure was not known.

Chemical analyses of several of the chromium compounds showed that their composition deviates from the formula ACr_2X_4 . Compositions of about $A_{0.75}Cr_2S_{3.75}$ [3], $Eu_{0.69}Cr_2S_{3.80}$ [5] and



were reported. Assuming A to be divalent and Cr to be trivalent (from magnetic measurements) we adopt the general formula $A_{1-p}Cr_2X_{4-p}$ with $p \approx 0.3$.

No systematic absences were found in X-ray diagrams of the hexagonal crystals; from the shortness of the c_0 axes and the observation that the intensity sequences of $(hk0)$ and $(hk2)$ reflections are not equal, Omloo *et al.* [3] concluded to the absence of a mirror plane perpendicular to c_0 and proposed space group P6. However, several attempts to determine the crystal structure of $A_{1-p}Cr_2X_{4-p}$, both in our laboratory and elsewhere, failed. In rotation diagrams taken about the c axis Omloo had observed weak and diffuse layer lines in addition to the *normal* layer lines. Since the spacings of the extra layer lines corresponded to the c axes of binary chromium sulfides [7] or selenides [8] it was assumed that these compounds were present as contaminants. Nguyen Huy Dung [6] also observed these extra layer lines and noted that they could be indexed by adopting a c axis equal to $5c_0$; he tentatively ascribed them to twinning.

In the present communication we report the structure of the compounds $A_{1-p}Cr_2X_{4-p}$ as determined by X-ray diffraction. The structures are of an entirely novel type consisting of three hexagonal units with common a and b axes, but with different — and mutually incommensurate — c axes. This symbiosis of three structural units, each ordered in its own way, is called *multiple order*. The ratio of the lengths of the three c axes determines the chemical composition of $A_{1-p}Cr_2X_{4-p}$; the values of p thus derived are of the order of 0.29.

Experimental. — Small needle-shaped crystals of $A_{1-p}Cr_2X_{4-p}$ were provided by Drs. J. Rijnsdorp (who studies their magnetic anisotropy); the crystals had been prepared by heating mixtures of the elements, containing an excess of the chalcogen, in thick-walled quartz tubes for several weeks at

1 000-1 300 °C ($X = S$) or 800-900 °C ($X = Se$).

Rotation diagrams about the c axis (needle axis), taken with $CuK\alpha$ (in some cases $MoK\alpha$) radiation, showed weak additional layer lines between the strong layer lines corresponding to a repeat distance of c_0^* . Analysis showed that there are three types of layer lines :

a) Strong layer lines with repeat distance c_0^* consisting of sharp spots; the observed layer lines correspond to reciprocal-lattice vectors $l_0 \cdot c_0^*$ with $l_0 = 0, 1, 2, 3$, etc.

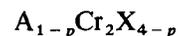
b) Weak diffuse layer lines with repeat distance c_0^* ; sometimes diffuse spots can be distinguished; these layer lines were observed with reciprocal-lattice vectors $l_6 \cdot c_0^*$ with $l_6 = 1, 2, 3$ and (in some cases) 4.

c) Weak layer lines consisting of sharp spots; for $Pb_{1-p}Cr_2S_{4-p}$ the reciprocal-lattice vectors of the

observed layer lines are c_3^* and $2c_3^*$; for the other compounds: c_3^* , $(c_0^* + c_3^*)$ and sometimes $(c_0^* - c_3^*)$.

The sharp spots of types a) and c) could also be observed on Weissenberg diagrams about the c axis and on powder diagrams ($CuK\alpha$ radiation), but the diffuse reflections of type b) were not observed by these techniques. Table I gives the values of a and c_0 from powder diagrams, of c_3/c_0 from powder and rotation diagrams and of c_6/c_0 from rotation diagrams only; the latter values presumably are less accurate.

$Ba_{1-p}Cr_2Se_{4-p}$ is an exception; here the spots of type b) are fairly sharp and observable in powder and Weissenberg diagrams; the ratios are: $c_3/c_0 = 5/4$ and $c_6/c_0 = 5/3$. For the other compounds



somewhat different and incommensurate values are found for the ratios c_3/c_0 and c_6/c_0 (Table I).

TABLE I

Unit-cell dimensions of the hexagonal compounds $A_{1-p}Cr_2X_{4-p}$

	a (Å)	c_0 (Å)	c_3/c_0	c_6/c_0	p^*
$Ba_{1-p}Cr_2S_{4-p}$	21.99	3.433	1.292	1.691	0.295
$Sr_{1-p}Cr_2S_{4-p}$	21.54	3.445	1.205	1.655	0.282
$Eu_{1-p}Cr_2S_{4-p}$	21.41	3.446	1.224	1.646	0.284
$Pb_{1-p}Cr_2S_{4-p}$	21.43	3.476	1.207	1.638	0.281
$Ba_{1-p}Cr_2Se_{4-p}$	22.93	3.620	1.250 (**)	1.667 (**)	0.288
$Sr_{1-p}Cr_2Se_{4-p}$	22.49	3.623	1.274	1.660	0.290
$Eu_{1-p}Cr_2Se_{4-p}$	22.43	3.622	1.272	1.649	0.289
$Pb_{1-p}Cr_2Se_{4-p}$	22.37	3.640	1.261	1.641	0.288

(*) Composition parameter calculated from c_3/c_0 and c_6/c_0 .
 (**) Commensurate.

Intensities of type a) and c) reflections were visually estimated from Weissenberg diagrams of several of the compounds; for $Ba_{1-p}Cr_2Se_{4-p}$ intensities of type b) reflections were also estimated. Accurate intensities of type a) reflections of $Eu_{1-p}Cr_2Se_{4-p}$ were measured by counter methods using an automatic three-circle goniometer (Nonius) with $MoK\alpha$ radiation; corrections for absorption were applied.

Structure determination. — Adopting space group P6 a three-dimensional Patterson synthesis of $Eu_{1-p}Cr_2Se_{4-p}$ was calculated from the structure factors of 335 independent $(hk0)$ and 664 independent (hkl_0) ($l_0 \neq 0$) reflections. No Eu-Eu vectors could be located in the map, but analysis of the Patterson peaks around the origin indicated that $CrSe_6$ octahedra sharing edges are an important feature of the structure. The positions of the octahedra could be determined by means of the implication method [9] making use of the threefold axes; they were refined by

Fourier methods. A framework of linked CrSe_6 octahedra was found which leaves wide channels around the sixfold and threefold axes (figure 1).

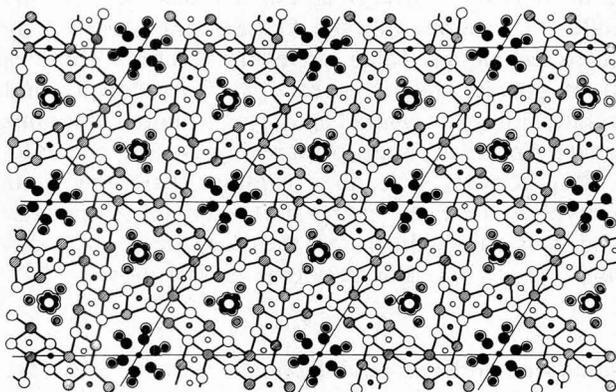


FIG. 1. — Projection of the structure of $\text{Eu}_{1-p}\text{Cr}_2\text{Se}_{4-p}$ on the hexagonal plane. Cr atoms are shown as small circles, Se as large circles, Eu as double circles. Open circles correspond to $z_0 = 0$, hatched circles to $z_0 = 1/2$, while black circles have no defined z_0 parameter.

The occupation of these channels could not be found by three-dimensional methods. A Fourier projection on the basal plane, however, revealed the atoms in the channels. The x, y parameters of all atoms and their occupation numbers were refined by least squares. While the occupation numbers of the framework atoms are unity, those of the atoms in the channels were found to be non-integral; moreover it was not yet known which of these atoms was Eu, which Se or possibly Cr. The final index R for the $(hk0)$ reflections was 3.2% ($R_w = 2.3\%$).

Refinement of the (hkl_0) ($l_0 \neq 0$) reflections led to positions of the framework atoms virtually identical with those derived from $(hk0)$ reflections. The z_0 parameters of these atoms did not significantly differ from 0 or 1/2, indicating that the framework has space group $P6/m$. For the atoms in the channels about the threefold axes also positions and occupancies close to those derived from $(kh0)$ reflections were found and z_0 parameters close to 0 or 1/2 (Table II). These atoms showed large pseudo-thermal motion, particularly in the c direction, the apparent r.m.s. deviations in that direction being about 0.3 Å (compared to 0.1 Å for the framework atoms). The atoms in the channels about the sixfold axis, however, were found not to contribute significantly to the (hkl_0) ($l_0 \neq 0$) reflections. (This explains that the intensity sequences for $l = 0$ and $l_0 = 2$ are different and also the failure to find Eu-Eu vectors in the three-dimensional Patterson maps.) The final index R for the (hkl_0) ($l \neq 0$) reflections was 5.2% ($R_w = 2.6\%$).

It seemed likely that the intermediate layer lines of type b) or c) are due to the atoms in the channels about the sixfold axis. From stereochemical arguments

TABLE II

Atomic positions and apparent occupation numbers in $\text{Eu}_{1-p}\text{Cr}_2\text{Se}_{4-p}$; standard deviations in units of the last decimal place are given in parentheses.

Framework; space group $P6/m$				
	occ. (*)	x	y	z_0
Cr1	1	1/2	0	1/2
Cr2	1	0.436 10(11)	0.101 36(11)	0
Cr3	1	0.374 21(11)	0.188 76(11)	1/2
Cr4	1	0.324 43(11)	0.296 45(11)	0
Se1	1	0.389 34(7)	0.005 08(7)	1/2
Se2	1	0.320 38(7)	0.097 85(7)	0
Se3	1	0.270 10(7)	0.207 74(7)	1/2
Se4	1	0.541 36(7)	0.090 26(7)	0
Se5	1	0.485 78(7)	0.188 34(7)	1/2
Se6	1	0.424 22(7)	0.277 86(7)	0

Channels about threefold axes					
	occ. (*)	x	y	z_0	z_3
Eu1	0.68	0.564 22(7)	0.351 88(7)	$\sim 1/2$	$\sim 1/2$
Eu11	0.04	0.655 2 (10)	0.289 7 (13)		
Eu12	0.04	0.678 2 (10)	0.376 9 (13)		
Se7	0.86	2/3	1/3	~ 0	~ 0

Channel about sixfold axis; space group $P6_3/m$				
	occ. (*)	x	y	z_6
Eu2	0.62	0.177 03(9)	0.053 58(9)	1/4
Cr5	1.28	0	0	0.1/2
Se8	0.66	0.105 53(17)	0.031 73(17)	3/4

(*) Apparent occupation number per unit c_0 .

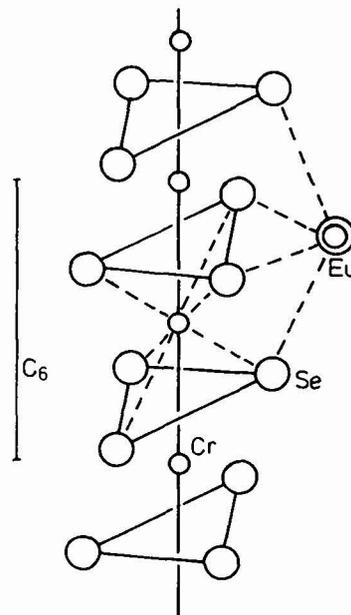


FIG. 2. — Structure of the chain about the sixfold (screw) axis of $\text{Eu}_{1-p}\text{Cr}_2\text{Se}_{4-p}$; only one of the Eu atoms of the chain is shown.

a model for the occupation of these channels was derived (figure 2) which led to reasonable interatomic

distances (Table III, figure 3) and to occupation numbers of 0.617 for Eu2, 0.659 for Se8 and

$$1.28 = 2 \times 0.64$$

for Cr5 in the $(hk0)$ projection. The weighed average of these numbers (0.626) is fairly close to the observed value of c_0/c_6 (0.606) indicating that the repeat distance for this model is c_6 and that the layer lines of type $b)$ are due to this part of the structure. Because of the diffuseness of these layer lines this hypothesis

TABLE III

Interatomic distances (in Å) in $Eu_{1-p}Cr_2Se_{4-p}$

Framework		Channels about threefold axes	
Cr1 - 2 Se1	2.54	Eu1 - 2 Se7	3.3
- 4 Se4	2.52	- Se4	} Fig. 4
Cr2 - 2 Se1	2.60	- Se5	
- 1 Se2	2.55	- Se6	
- 1 Se4	2.49		
- 2 Se5	2.48		
		Channel about sixfold axis	
Cr3 - 2 Se2	2.53		
- 1 Se3	2.58	Eu2 - 1 Se8	3.07
- 1 Se5	2.50	- 1 Se8	3.08
- 2 Se6	2.51	- 2 Se8	3.31
Cr4 - 2 Se1	2.58	- Se2	} Fig. 3
- 1 Se2	2.60	- Se3	
- 2 Se3	2.50		
- 1 Se6	2.47	Cr5 - 6 Se8	2.58
Cr2 - 1 Cr4	3.02	Cr5 - 2 Cr5	2.99

could not be tested for $Eu_{1-p}Cr_2Se_{4-p}$, but it was tested and fully confirmed for $Ba_{1-p}Cr_2Se_{4-p}$. The diffuseness of type $b)$ reflections for the other compounds shows the absence of correlation of the z parameters of the atoms about the sixfold axes in different unit cells and with the framework atoms.

It now seemed natural to correlate reflections of type $c)$ with the occupancy of the channels about the three-fold axes. Indeed, for $Pb_{1-p}Cr_2S_{4-p}$ very much the same reasoning applies as was just given above, leading to a simple model for the occupancy of these channels, viz. a chain of trigonal prisms A_6X sharing triangular faces with repeat distance c_3 . For the other compounds $A_{1-p}Cr_2X_{4-p}$ the situation is more complicated as is shown by the observation of layer lines with reciprocal-lattice vectors $c_0^* - c_3^*$ and $c_0^* + c_3^*$. The sharpness of the *satellite* reflections forming these layer lines indicates that the arrangement of the atoms about the threefold axes is strongly modulated by the framework (and *vice versa*). A model for this modulation will be discussed below.

Discussion. — The structure of $A_{1-p}Cr_2X_{4-p}$ (figure 1) may be described as an intergrowth of three units, viz. the three-dimensional framework and the one-dimensional chains about the sixfold and threefold axes, respectively. These three units have a common hexagonal basal plane, but different c axes; their space groups and the atomic parameters in $Eu_{1-p}Cr_2Se_{4-p}$ are given in table II, short interatomic distances in table III and figures 3 and 4.

The framework built by linked CrX_6 octahedra has composition $Cr_{21}X_{36}$ (with formal charge -9) per repeat distance c_0 . In most cases the octahedra are linked by common edges to form lath-shaped platelets (infinite in the c direction). The octahedra about Cr2 and Cr4 share a common face, thus joining the platelets to form the three-dimensional framework. Somewhat similar frameworks have been found in $TiCr_3S_5$,

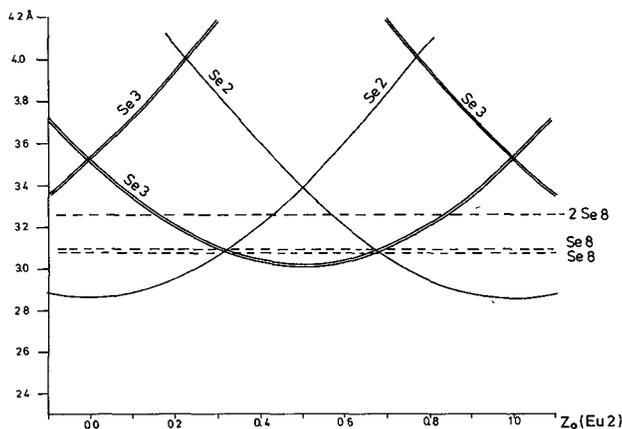


FIG. 3. — Distance of Eu2 (in the chain about the sixfold axis) from Se8 (in the same chain) and Se2 and Se3 (in the framework) as a function of its z_0 parameter; all values of z_0 are possible.

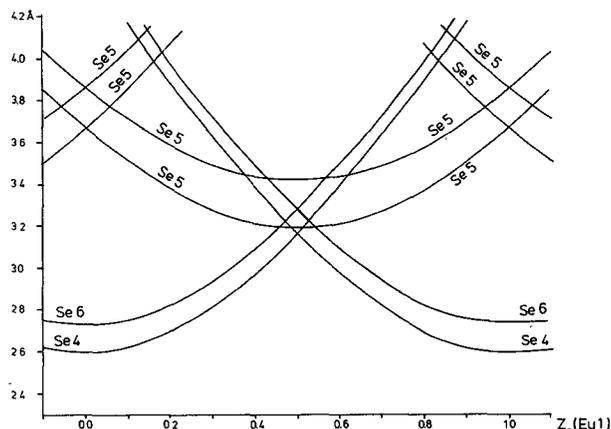


FIG. 4. — Distance of Eu1 (in the chains about the threefold axes) from the framework atoms Se4, Se5 and Se6 as a function of its z_0 parameter; this parameter will lie in the range 0.3-0.7.

TlCr₃Se₅ [10] and TlV₅S₈ [11]. In these compounds the channels in the framework are occupied by Tl, in A_{1-p}Cr₂X_{4-p} by more complex units.

The units about the sixfold axis have space group P6₃/m; they consist of a chain of CrX₆ octahedra sharing faces, which is surrounded by A cations; this results in a composition A₆Cr₂X₆ (with formal charge + 6) per repeat distance c₆. This repeat distance corresponds to twice the thickness of a CrX₆ octahedron, while c₀ corresponds to an octahedron edge. For ideal octahedra, therefore, a ratio

$$c_6/c_0 = \sqrt{8/3} = 1.633$$

is expected; the observed values (Table I) are close to this *ideal* value. In Eu_{1-p}Cr₂Se_{4-p} the Eu2 cations are coordinated by 4 Se8 in the chain (figure 2) and by 3 to 5 Se2 and Se3 atoms of the framework. The projections of the Eu2-Se2 and Eu2-Se3 distances on the basal plane (figure 1) are almost equal and any value of the z₀ parameter of Eu2 leads to reasonable distances of this atom to the Se atoms of the framework (figure 3). The lack of correlation of the z parameters of the Eu₆Cr₂Se₆ chain with the framework can thus be understood.

A different situation holds for the chains about the threefold axes which have an ideal composition of Eu₃Se (formal charge + 4) per repeat distance c₃. This repeat distance probably is determined by the Eu1-Eu1 contacts in the c direction. However, the framework atoms Se4 and Se6, which are coordinated at Eu1, confine its z₀ parameter to the range of about 0.3-0.7 (figure 4). This leads to the observed correlation of the z parameters of the chain with the framework and to a modulation of the chain structure by the framework (and *vice versa*) with a reciprocal modulation vector equal to c₀^{*} - c₃^{*}. A model for this modulation is depicted in figure 5. This model explains the large apparent thermal motion of the atoms in the chain (particularly in the c direction) and the observation of the alternative, weakly occupied sites Eu11 and Eu12. Sterical hindrance among these sites probably causes a slight deficit of Eu relative to the *ideal* composition Eu₃Se for the chain.

The failure of the electroneutrality condition

$$-9/c_0 + 6/c_6 + 2 \times 4/c_3 = 0$$

to hold exactly for the observed values of c₆/c₀ and c₃/c₀ also indicates a small deficit of cations in some site of A_{1-p}Cr₂X_{4-p}. Assuming this deficit to be in A sites, the values of p in the formula can be calculated from the observed values of c₆/c₀ and c₃/c₀. The results are included in table I.

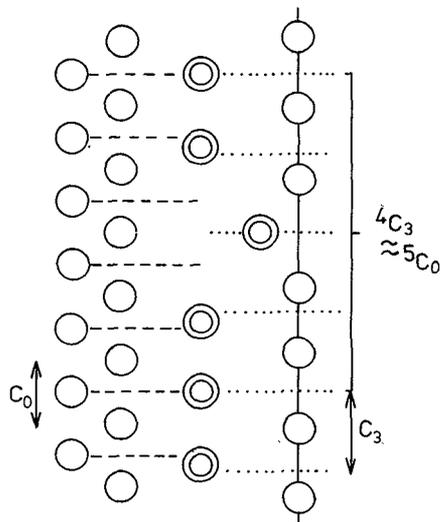


FIG. 5. — A model for the modulation of one chain about a threefold axis (right-hand side) by the framework (left-hand side of the figure); open circles are Se, double circles Eu. The z₀ parameters of the Eu1 atoms are a compromise between the requirements (broken lines) of the selenium atoms in the framework and the chain repeat distance c₃ (dotted lines). Where no compromise is possible (middle of the figure), an alternative site Eu11 or Eu12 is occupied. The Se7 atoms on the threefold axis follow the modulation of the Eu positions. Actual values for c₃/c₀ are incommensurate.

Some features of the structure (and the X-ray diffraction patterns) of A_{1-p}Cr₂X_{4-p} are reminiscent of inclusion compounds, for instance of urea with organic molecules [12]. In these inclusion compounds both the host and the inserted molecules are neutral compounds which can exist by themselves. This is not so for the compounds A_{1-p}Cr₂X_{4-p} where neither the framework, nor the chains can exist without one another. We therefore regard the structure of A_{1-p}Cr₂X_{4-p} as an entirely novel type of crystal structure which may be called a *multiple-order structure* or perhaps an *intergrowth structure*.

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