Intergrowth Structure of $Eu_{1-p}Cr_2Se_{4-p}$ ($p = 0\cdot29$) and Isotypic Compounds. A Novel Type of Crystal Structure with Three Incommensurate Periodicities in One Direction: *X*-Ray Study

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Summary The structure of the compounds $A_{1-p}Cr_2X_{4-p}$ (A = Pb, Eu, Sr, or Ba; X = S or Se), as determined by *X*-ray diffraction, consists of three structural units which have a common hexagonal basal plane, but different, mutually incommensurate *c*-axes.

IN 1968 Omloo *et al.*[1] reported the synthesis and some properties of a series of hexagonal compounds to which the formula ACr_2X_4 was assigned, where A is a large divalent cation (Pb, Eu, Sr, or Ba) and X is S or Se. The interesting magnetic properties of these semiconducting compounds, in particular of the Eu derivatives, have received considerable attention, both in our laboratory[2] and elsewhere. However, the interpretation of these properties was hampered by uncertainties about the exact composition of the compounds and by the fact that their crystal structure was not known. Assuming A to be divalent and Cr trivalent (from magnetic measurements) the results of several chemical analyses [2–4] can best be represented by the general formula $A_{1-p}Cr_2X_{4-p}$ with *p ca.* 0·3.

We now report the crystal structure of $A_{1-p}Cr_2X_{4-p}$, as determined by *X*-ray diffraction. The structure is of an entirely novel type; it may be described as an intergrowth of three structural units which have a common hexagonal basal plane, but different and mutually incommensurate *c*-axes (Table).

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

Compound	a_0/Å	c_0/Å	$c_3 : c_0$	$c_6 : c_0$	p^a
$Pb_{1-p}Cr_2S_{4-p}$	21·43	3·476	1·207 : 1	1·638 : 1	0·281
$Eu_{1-p}Cr_2S_{4-p}$	21·41	3·446	1·224 : 1	1·646 : 1	0·284
$Sr_{1-p}Cr_2S_{4-p}$	21·54	3·445	1·205 : 1	1·655 : 1	0·282
$Ba_{1-p}Cr_2S_{4-p}$	21·99	3·433	1·292 : 1	1·691 : 1	0·295
$Pb_{1-p}Cr_2Se_{4-p}$	22·37	3·640	1·261 : 1	1·641 : 1	0·288
$Eu_{1-p}Cr_2Se_{4-p}$	22·43	3·622	1·272 : 1	1·649 : 1	0·289
$Sr_{1-p}Cr_2Se_{4-p}$	22·49	3·623	1·274 : 1	1·660 : 1	0·290
$Ba_{1-p}Cr_2Se_{4-p}$	22·93	3·620	1·250 : 1^b	1·667 : 1^b	0·288

[a] Composition parameter calculated from ratios of $c_3 : c_0$ and $c_6 : c_0$. [b] Commensurate.

Rotation diagrams about the *c*-axis of the needle-shaped crystals show three types of layer lines: (a) strong layer lines consisting of sharp spots corresponding to reciprocal-lattice vectors $l_0 . c_0{}^*$ with l_0 = 0,1,2,3, *etc.*, (b) weak diffuse layer lines, in some cases with diffuse spots; these layer lines have reciprocal-lattice vectors $l_6 . c_6{}^*$ with l_6 = 1,2,3,4, and (c) weak layer lines consisting of sharp spots; the reciprocal-lattice vectors of these layer lines are $c_3{}^*$, $(c_0{}^* + c_3{}^*)$ and in some cases $(c_0{}^* - c_3{}^*)$.

The compounds $Pb_{1-p}Cr_2S_{4-p}$ and $Ba_{1-p}Cr_2Se_{4-p}$ are somewhat exceptional. For $Pb_{1-p}Cr_2S_{4-p}$ type (c) layer lines are observed with reciprocal-lattice vectors $c_3{}^*$ and $2c_3{}^*$. For $Ba_{1-p}Cr_2Se_{4-p}$ type (b) layer lines show fairly sharp spots, while c_0, c_3, and c_6 are commensurate ($c = 5c_0 = 4c_3 = 3c_6$). For the other compounds the ratios $c_3 : c_0$ and $c_6 : c_0$ are somewhat different and incommensurate (Table).

Accurate intensities of type (a) reflections of $Eu_{1-p}Cr_2Se_{4-p}$ were measured by counter methods and corrected for absorption. Furthermore, intensities of types (a) and (c) reflections of several of the compounds were visually estimated from Weissenberg diagrams; for type (b) reflections this was possible for $Ba_{1-p}Cr_2Se_{4-p}$ only.

The determination of the structure of $Eu_{1-p}Cr_2Se_{4-p}$ which included some rather unusual steps, will be reported elsewhere; after refinement the index *R* for 335 independent (*hk*0) reflections was 3·2% (R_W = 2·3%) and for 664 independent (hkl_0) ($l_0 \neq 0$) reflections 5·2% (R_W = 2·6%). A projection of the structure is shown in Figure 1. Three structural units can be distinguished:

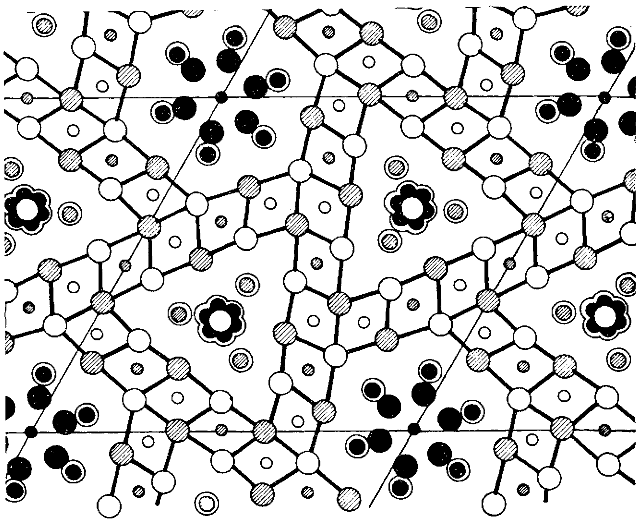

FIGURE 1. Projection of the structure of $Eu_{1-p}Cr_2Se_{4-p}$ on the hexagonal plane. Cr atoms are shown as small circles, Se as large circles, Eu as double circles. Open circles correspond to $z_0 = 0$, hatched circles to $z_0 = \frac{1}{2}$, while black circles have no defined z_0 parameter.

(1) A three-dimensional framework formed by CrX_6 octahedra sharing edges and faces which leaves wide channels about the six-fold and three-fold axes. The repeat distance of the framework in the *c* direction is c_0, the unit-cell content is $Cr_{21}X_{36}$ per repeat distance c_0, and the space group of the framework is $P6/m$.

(2) The channels about the six-fold axis are occupied by chains of composition $A_6Cr_2X_6$ per repeat distance c_6; these chains are formed by CrX_6 octahedra sharing faces which are surrounded by the A cations (Figure 2). The space group of these units is $P6_3/m$. Since c_6 is twice the thickness of a CrX_6 octahedron, while c_0 corresponds to an octahedron edge, the ideal value of $c_6 : c_0$ would be $\sqrt{8/3}$ = 1·633 : 1 (*cf.* Table).

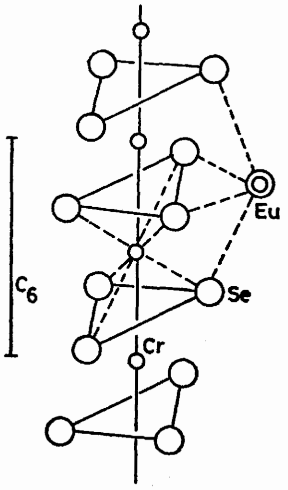

FIGURE 2. Structure of the chain about the six-fold (screw) axis of $\mathrm{Eu}_{1-p}\mathrm{Cr}_2\mathrm{Se}_{4-p}$; only one of the Eu atoms of the chain is shown.

(3) The channels about the threefold axes contain chains of composition $\mathrm{A}_3\mathrm{X}$ (probably with a slight deficit of A) per repeat distance c_3. These chains are based on trigonal prisms $\mathrm{A}_6\mathrm{X}$ sharing triangular faces, but they are strongly modulated by the framework. A model for this modulation is shown in Figure 3.

While all three structural units contribute to the reflections ($hk0$), the reflections (hkl_0) with $l_0 \neq 0$ are due to the atoms of units (1) and (3) only, the latter with large quasi-thermal displacements in the c direction. The diffuse reflections of type (b) are due to structural unit (2) and the sharp reflexions of type (c) are mainly due to structural units (3). These observations indicate that the z parameters of the chains (2) in different unit cells are not correlated with each other (except for $\mathrm{Ba}_{1-p}\mathrm{Cr}_2\mathrm{Se}_{4-p}$) or with the framework. However, chains (3) are correlated with the framework and modulated by it (except for $\mathrm{Pb}_{1-p}\mathrm{Cr}_2\mathrm{S}_{4-p}$), as shown by the satellite reflections with $(c_0^* + c_3^*)$ and $(c_0^* - c_3^*)$.

The chemical composition of the compounds $\mathrm{A}_{1-p}\mathrm{Cr}_2\mathrm{X}_{4-p}$ is determined by the axial ratios $c_6 : c_0$ and $c_3 : c_0$; calculated values of p are included in the Table. Although the structure of $\mathrm{A}_{1-p}\mathrm{Cr}_2\mathrm{X}_{4-p}$ has some features in common with those of inclusion compounds, *e.g.* of urea with organic molecules,[5] it is sufficiently different to be regarded as an entirely novel type of crystal structure for which the name 'intergrowth structure' is proposed.

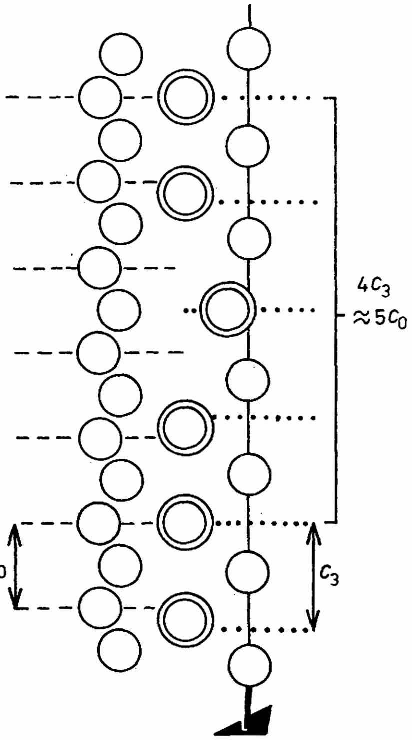

FIGURE 3. A model for the modulation of the chain about a three-fold axis (right-hand side) by the framework (left-hand side of the figure); open circles are Se, double circles Eu. The z_0 parameters of the Eu atoms are a compromise between the requirements (broken lines) of the Sc atoms in the framework and the chain repeat distance c_3 (dotted lines). Where no compromise is possible (middle of the figure), an alternative Eu site is occupied; *ca.* 10% of the Eu atoms in the chain are found on such sites. The Se atoms on the three-fold axis follow the modulation of the Eu positions. Actual values for $c_3 : c_0$ are incommensurate.

We thank Dr. J. Rijnsdorp for providing the crystals of $\mathrm{A}_{1-p}\mathrm{Cr}_2\mathrm{X}_{4-p}$ and the Crystal-Chemistry group of this University for the use of their X-ray diffraction equipment and computer programs. This investigation was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

(*Received*, 23*rd August* 1977; *Com.* 893.)

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