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Vacancy Ordering in $Y_{18}B_4\square_2Al_6S_{42}$ (B = Al, Sc) Compounds by HRTEM*

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Flahaut [1] has described a family of 250 compounds, $R_6(B_n\square_{2-n})C_2X_{14}$ (where R = La–Lu, Y; B and C = cations in octahedral and tetrahedral coordination respectively; X = S, Se). The parent structure has been described by Hyde *et al.* [2] in a very elegant way as the stuffed anti-Ru_7B_3-type. The great number of compounds is due to the coordination change of the **B** atom when moving along the $\bar{6}$ axis and the balance of charges between the **B** and C cations.

It has been claimed [1] that a superstructure of the basic hexagonal cell only takes place if the ratio between the number of vacancies and the **B** cations is greater than one.

In this work we present preliminary results concerning the modulate structure (commensurate) of compounds $Y_{18}B_4\square_2Al_6S_{42}$ (B = Al, Sc) where the ratio between the empty and the occupied **B** positions is smaller than one.

The close structural analogy between the $YScS_3$ phase [3], the stuffed anti-Fe_3C structural type and the Ru_7B_3-type (see ref. 2) suggest the possibility of intergrowths. For this reason we have prepared mixtures of both types of sulphides in variable proportions.

Experimental

Sample Preparation

The compound $Y_{18}Al_{10}\square_2S_{42}$ (**P**) was prepared by heating a carbon crucible containing $9Y_2S_3$ + 10Al in a stream of H_2S + Ar at 1873 K (75 min); the mixture was homogenised and heated again at 1573 K (30 min), then slowly cooled to room temperature. The orthorhombic phase $YScS_3$ (**Q**) was prepared in the same way from the binary sulphides. Mixtures of both compounds in different ratios (**P**:**Q**) (3:1; 1:1; 2:3; 1:2) were also prepared. The (1:1) mixtures were annealed at 1373 K (62 days) in evacuated sealed silica tubes and cooled slowly or quenched to room temperature.

X-ray Diffraction/Electron Microscopy

A Guinier–Hägg (XDC-700) camera with Cu $K\alpha_1$ = 1.5405981 Å and Si (National Bureau Standards) a_o = 5.4305(1) Å was used.

Electron diffraction patterns and micrographs were performed on Jeol 100 CX and 200 CX microscopes.

Results and Discussion

The unit cell parameters for the **Q** phase were a = 7.0020(8) Å, b = 9.478(1) Å, c = 6.3727(8) Å, V = 423.0(1) $Å^3$, in good agreement with ref. 3. The X-ray powder pattern from the **P** sample was very complex, with ~100 reflections present in the range $5° < 2\theta < 90°$. Most of the observed maxima (60) could be indexed in a hexagonal cell [1], with parameters a_o = 9.5903(8) Å, c_o = 6.070(1) Å, V = 483.6(1) $Å^3$, but ~40 reflections remain unassigned. Nevertheless, transmission electron microscopic studies reveal directly a different unit cell. Figure 1 shows a set of electron diffraction patterns from the same crystal flake of this sample. We observed two types of reflections: (a) main reflections of strong intensity, subscript o, characteristic of the basic hexagonal cell; (b) superlattice spots of weak intensity, subscript s, giving rise to the new unit cell with $a_s = \sqrt{3}a_o$ = 16.958(3) Å, $c_s = 3c_o$ = 18.294(6) Å, V = 4364(2) $Å^3$ (values refined from the X-ray data).

The analysis of the whole observed diffraction patterns suggest the possibility of rhombohedral symmetry for the new cell, with the reflection conditions as follows: hkl, $\bar{h}+k+l = 3n$; $h\bar{h}l$, $h+l = 3n$; hhl, $l = 3n$; 001, $l = 3n$. The space group could be one of these: R_3, $R_{\bar{3}}$, R_{32}, R_{3m} or $R_{\bar{3}m}$, but X-ray single crystal studies are necessary.

On the other hand, the presence of intergrowths of the two phases **P** and **Q** was not observed. Mixtures of both compounds always appear in each of these preparations, with small variations in the unit cell parameters due to the possible substitution of Al^{3+} by Sc^{3+} in the octahedral positions.

Figure 2 corresponds to a high-resolution structure image from one crystal of the sample (3:1) of the hexagonal phase along the $[011]_o$ axis, see the inset; the contrast reveals a well-ordered material with the commensurate modulate structure indicated by

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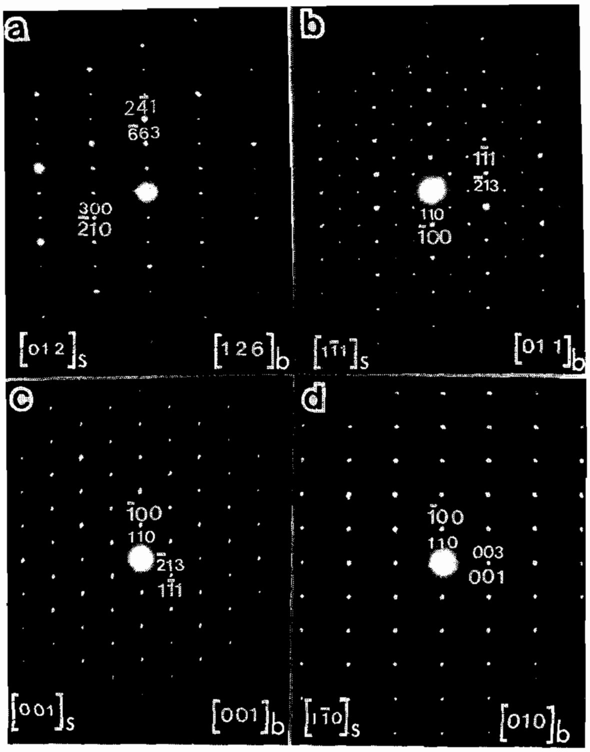

Fig. 1. Selected area diffraction patterns from the same crystal of sample $Y_{18}Al_{10}\square_2S_{42}$.

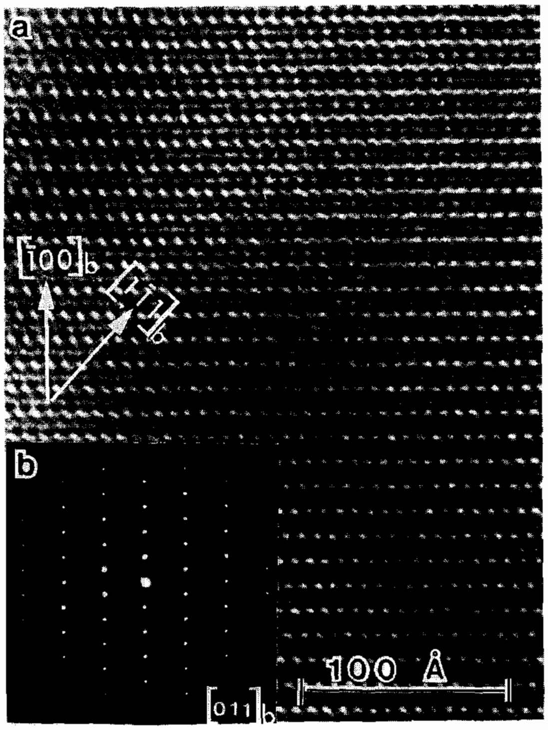

Fig. 3. (a) $[011]_o$ structure image from one crystal, hexagonal phase, of the (1:1) quenched sample; note the absence of superlattice spots (b).

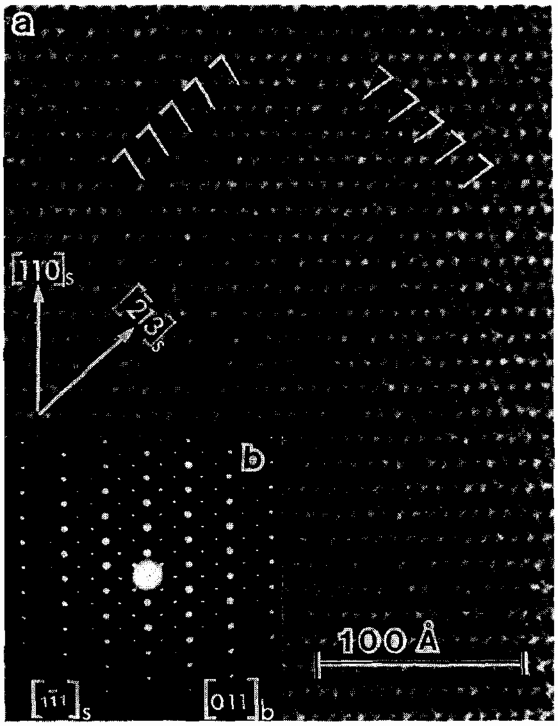

Fig. 2. (a) High-resolution structure image from one crystal of the sample (3:1), corresponding to the hexagonal phase; (b) incident beam is parallel to $[1\bar{1}1]_s = [011]_o$.

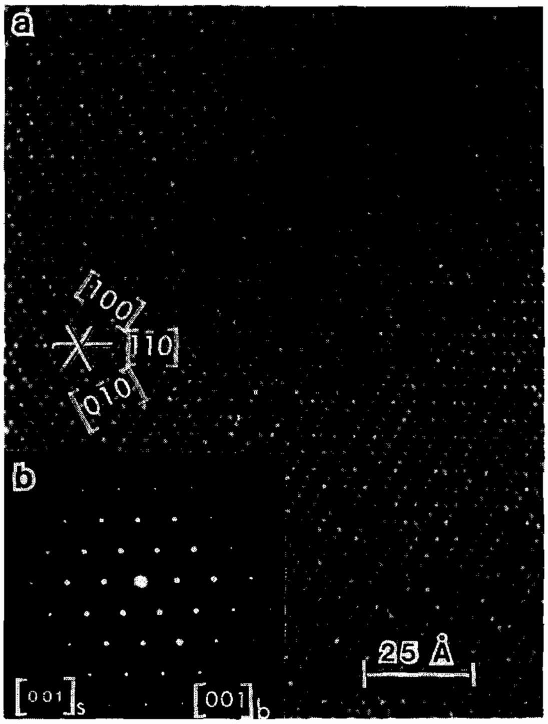

Fig. 4. (a) High resolution image along *c* axis; see diffraction pattern on the inset (b) from a crystal of the slowly cooled (1:1) sample.

arrows. The origin of this superstructure is due to the ordering of the B sites, occupied and vacant, along $\bar{6}$-fold axis. Structure images taken from some crystals of the same phase in the quenched (1:1) sample show the absence of superlattice spots, suggesting disorder on the B positions at high temperature; see, for example, Fig. 3 and compare it to Fig. 2.

The contrast observed in the high-resolution image along the *c* axis of the hexagonal phase (see Fig. 4) is very similar to the one observed by Amelinckx *et al.* [4] in clusters of M_7C_3 (M = Fe, Mn, Cr). Different ways of orientation of the trigonal prismatic sites (Y positions) or an ordering on this XY plane of the B cations and vacancies can give rise to the new parameter $a_s = \sqrt{3}a_o$; but this contrast is not evident from the micrograph along this projection.

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