The Structure of Defect Ru_4Si_3

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The nature of the defect structure of Ru_4Si_3 has been studied with electron diffraction and electron microscopy methods. Lattice image pictures, interpreted with histogram analysis, reveal that planar defects of chemical twinning type are common in the crystals.

Chemical twinning, or twinning on the unit cell level was recently proposed to be an important new mechanism of nonstoichiometry (*1*). It was also shown that the structure types of Rh_5Ge_3 (*2*) and Ru_4Si_3 (*3*) could be derived by chemical twinning operations (*1*). The relationships between several structures of compounds in the Ru–Si system, Ru_2Si, Ru_5Si_3 (isostructural with Rh_5Ge_3), Ru_4Si_3 and RuSi were described earlier by Engström (*4*). In order to illuminate the principles of chemical twinning with an experimental example, we have chosen to study the compound Ru_4Si_3 with modern electron microscopy methods.

Experimental Methods

The original sample which was prepared by arcmelting a mixture of Ru and Si and followed by heat treatment at 1400°C, and used for finding crystals suitable for the X-ray crystal structure determination (*3*) was also used in this investigation. The X-ray powder pattern showed minor amounts of Ru_5Si_3 to be present. A small portion of the sample was ground and collected on thin perforated carbon films, and examined in a Philips EM 301 G electron microscope operated at 100 kV. It was rather difficult to find good crystals, normally only one or two were found during several hours' search. Crystals were aligned with their *b*-axes parallel to the electron beam, and with a number of *h0l* reflexions operating, lattice images were easily observed. A typical example is given in Fig. 1, which represents a tip of a crystal, and fringes separated by 17 Å corresponding to the *c*-axis are clearly visible. Separations between fringes were measured with a microdensitometer to an accuracy of ±0.3 Å obtained from a histogram analysis.

Results

Typical lattice image pictures are shown in Figs. 2a and 2b. Planar defects revealed by an eye inspection are rare, one is demonstrated in Fig. 2b. In this case of chemical twinning, the calculated variation in spacing is only slightly more than one Å (see below) and with an average spacing of 17 Å as present in
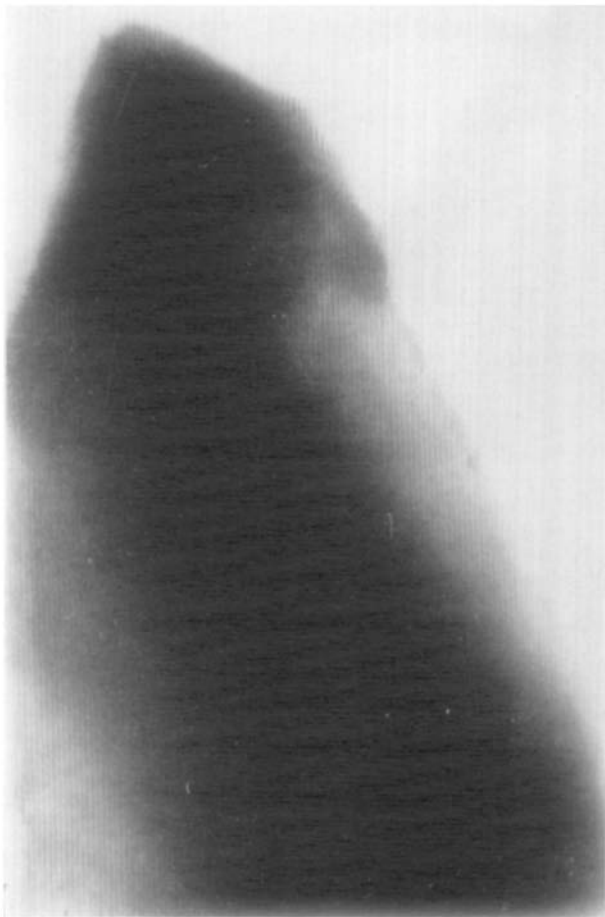
FIG. 1. Crystal tip of Ru₄Si₃ with one dimensional images, corresponding to the c-axis of 17 Å.

R₄Si₃, it could be that an eye inspection was not enough to describe the possible non-stoichiometry of a crystal of Ru₄Si₃. A number of microdensitometer recordings were thus carefully measured on five different crystals, one typical being shown in Fig. 3 with measured spacings given as fractions of c in Ru₄Si₃. These observations are plotted in a histogram in Fig. 4, and it is very clear that on both sides of the strong peak at 17 Å, representing c in Ru₄Si₃, a number of smaller peaks appear at regular intervals.

The twin blocks of the CsCl structure type present in the Ru₄Si₃ structure can be varied in size as is illustrated in Fig. 5. Figure 6 gives the structure of Ru₄Si₃. This gives us a num-ber of possible compounds of the general composition Ru_nSi_{n-2} as was shown by Engström (4) with the known examples Ru_2Si ($n = 4$), Ru_5Si_3 ($n = 5$), Ru_4Si_3 ($n = 8$), and RuSI ($n = \infty$). The c-axis of Ru₄Si₃ and the b-axis of Ru₅Si₃ are then even multiples $2n - 2$ of the interplanar spacing d of the (211) plane in a CsCl-type structure. This spacing was derived to be 1.229 Å from the observed unit cell dimensions of Ru₄Si₃ and Ru₅Si₃. Odd multiples correspond to regular one to one intergrowth structures. It must also be kept in mind that odd or even multiples of $2n - 2$ also can be explained by various twin intergrowth.
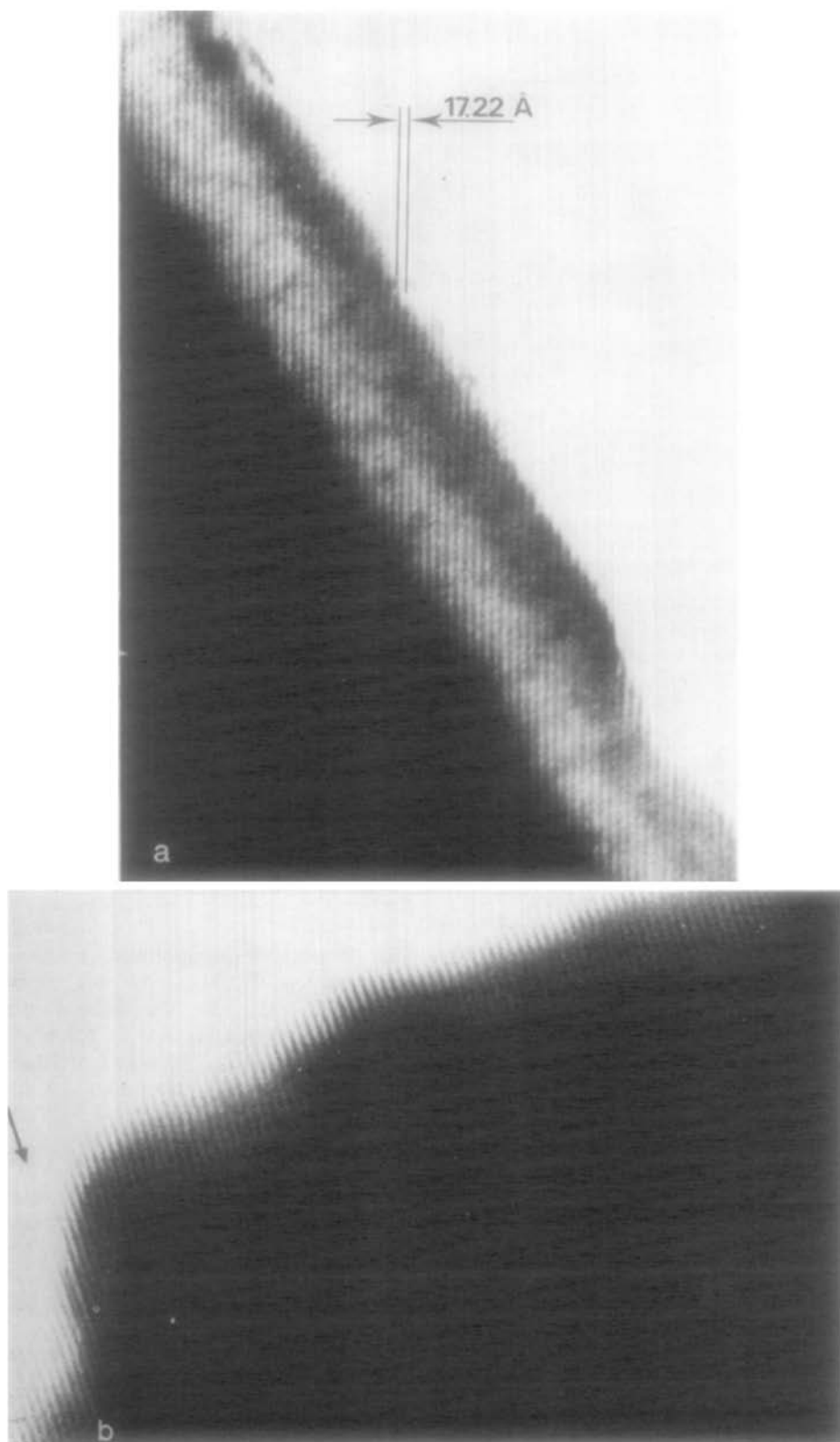
In this way calculated spacings for twin

FIG. 2. Typical lattice images of crystals of Ru_4Si_3. One extended defect is shown by the arrow in Fig. 2b.
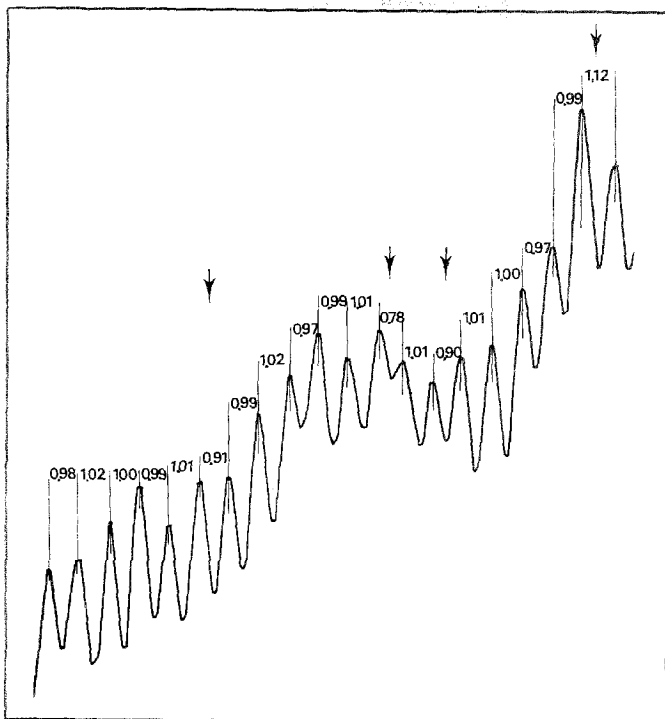
FIG. 3. Scanning profile of fringes perpendicular to c as obtained by a microdensitometer. The figures are measured distances between fringes in parts of c, where $c = 17.13$ Å. Arrows show four distances, which are significantly different from the "normal" distance of 17.13 Å.
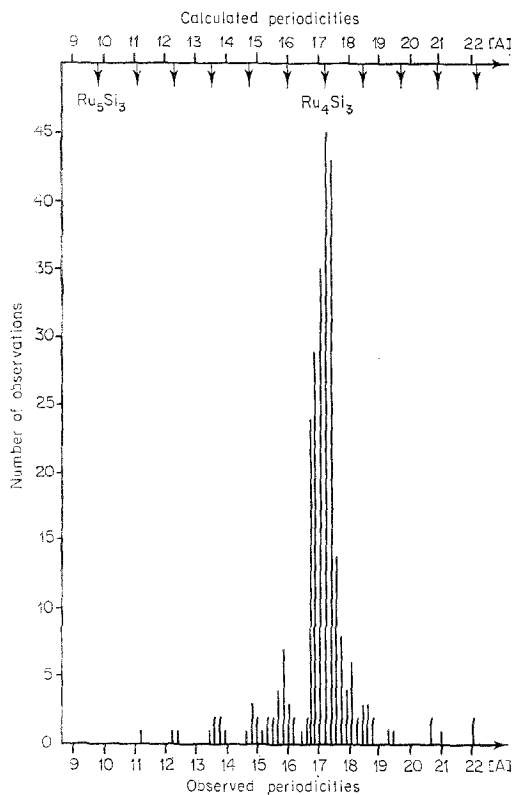

FIG. 4. Number of observations of distances between fringes perpendicular to c as measured on five crystals. The observed distances are to be compared with calculated distances between chemical twin planes as indicated by arrows in the upper part of the figure. Compare also Table I.
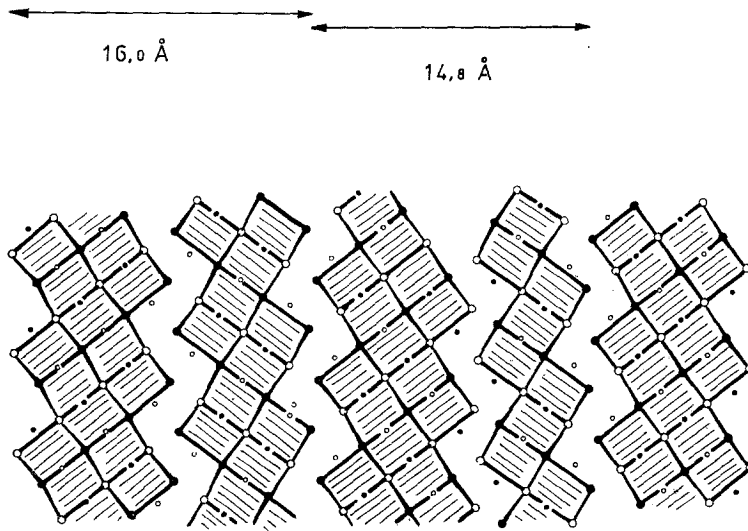
16,0 Å

14,8 Å

FIG. 5. Various block of the CsCl structure twinned to give structures related to Ru_4Si_3.
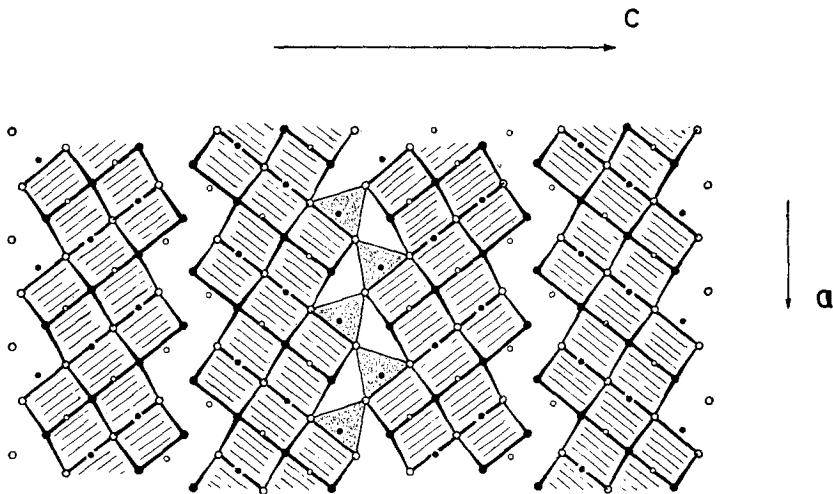
C

a

FIG. 6. The structure of Ru_4Si_3.

structures are obtained, and compared with the observed fringe spacings. This is done in Table I, the observed data are obtained from Fig. 4. Those given for Ru_2Si, Ru_5Si_3 and Ru_4Si_3 are naturally the ones from X-ray data (4). The excellent agreement between observed and calculated data of Table I and Fig. 4 does indeed reveal that the structure of defect Ru_4Si_3 is very well explained by chemical twinning. It is also clear from the

histogram of Fig. 4 that those five crystals have an overall composition of Ru_4Si_{3-x}, which is in agreement with the X-ray powder analysis.

A histogram analysis was also carried out on only one crystal and the result is shown in Fig. 7 together with calculated spacings in the top of the figure. Again the agreement is excellent, and the composition is again Ru_4Si_{3-x}.

TABLE I[a]

	$2n-2$	$d(2n-2) =$ Calculated spacings	Observed spacings	No. of observations
Ru_3Si	4	4.92		
	(5)	6.15		
$\underline{Ru_4Si_2}$	6	7.37	7.42*	—
	(7)	8.60	8.3	1
$\underline{Ru_5Si_3}$	8	9.83	8.82*	—
	(9)	11.06	11.2	1
Ru_6Si_4	10	12.29	12.3	2
	(11)	13.52	13.6	6
Ru_7Si_5	12	14.75	14.9	7
	(13)	15.98	15.8	20
Ru_8Si_6	14	17.21	17.13*	>200
	(15)	18.44	18.6	10
Ru_9Si_7	16	19.66	19.4	2
	(17)	20.89	20.8	3
$Ru_{10}Si_8$	18	22.12	22.1	2
⋮				
Ru_nSi_{n-2}				
⋮				
RuSi				

[a] Comparison of observed and calculated spacings for fringes observed in various crystals of Ru_4Si_3. d is the interplanar spacing of the (211) plane in a cubic structure of $a = 3.01$ Å, derived from the observed unit cell dimensions of Ru_4Si_3 and Ru_5Si_3. Underlined formulas are observed compounds in the Ru–Si system. Values marked with * are from X-ray data.
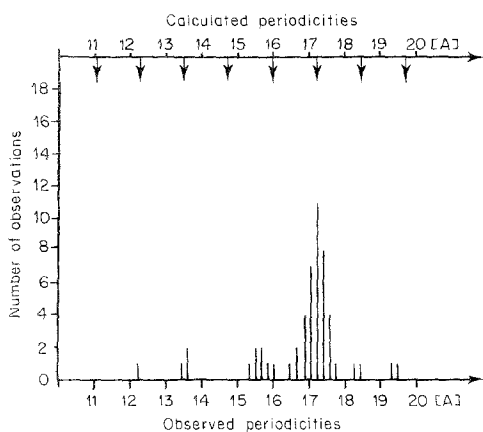

FIG. 7. Number of observations of distances between fringes perpendicular to c as measured on one crystal. The observed distances are to be compared with calculated distances between chemical twin planes as indicated by arrows in the upper part of the figure.

Extended planar defects of chemical twinning type cause non-stoichiometry in a crystal; the actual composition of the crystals investigated here has been calculated from the histogram analysis to be $Ru_4Si_{2.983}$, with an estimated error of .003. However, we cannot of course exclude the possibility of a classical Hägg nonstoichiometry mechanism, with partial occupancy of silicon in the two kinds of polyhedra that build the structure of Ru_4Si_3. Hägg nonstoichiometry is indeed very common and planar defects of chemical twinning type could exist together with partial occupancy of silicom atoms in one structure. This would change the composition of the crystals even more and would also change the unit cell dimensions. No such changes were possible to measure and we are inclined to believe that in the case of Ru_4Si_3, chemical

twinning gives the important mechanism for explaining the nature of the structure of defect Ru_4Si_3.

Acknowledgments

References

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