THE ORDERING OF THE SIGMA PHASE $V_{62}Co_{38}$ (*)

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ABSTRACT — The σ-phase structure $V_{62}Co_{38}$ has been studied using an X-ray single-crystal diffractometer. Both size and electronic factors appear to account for a complete ordering of this phase which is approximately stoichiometric. However a significant departure from complete ordering has been detected. [Crystal data: space group $P4_2/mmm$, $a = b = 8.834 \pm 0.004$, $c = 4.586_5 \pm 0.002$ Å].

1 — INTRODUCTION

The σ-phase structure has thirty atoms per unit cell distributed amongst sites ($2A + 8I_1 + 8I_2 + 8J + 4G$) of coordination numbers 12 (A, I_1), 14 (I_2, J) and 15 (G). The occupancies of the different atomic positions have been attributed to the following two factors: the electron concentration and the sizes of the constituent atoms. A review of previous works and a detailed description of ordering schemes is given in a recent paper [1].

The study of the σ-phase in the (V, Co) system is of interest owing to the wide composition range, 45 to 66 at % V [2], thus enabling a study of composition influence on ordering. The present work is concerned with the study of the ordering of an alloy at the V-rich end of the composition range.

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2 — EXPERIMENTAL

A single crystal was taken from an ingot of $V_{62}Co_{38}$, kindly supplied by Dr. J. M. Welter, from IFF/KFA, Julich, West Germany. A CAD4 diffractometer (Ag radiation) was used to measure the intensities. The lattice parameters were calculated using the least-squares method developed for the CAD4, as:

$$a = b = 8.834 \pm 0.004 \quad , \quad c = 4.586_5 \pm 0.002 \text{ Å}$$

3 — REFINEMENT

A statistical method developed by Gonschorek [3] was applied to select the 128 independent reflections used in the refinement. The selected reflections were corrected for Lorentz and polarization factors; these data were processed using the SDP CAD4 facilities. An isotropic temperature factor of 0.4 was used and no evidence of extinction was detected; no absorption correction was applied since this effect is likely to be small owing to the shape and small size of the crystal and to the radiation used.

The position parameters (Table 1) were refined from an initial set obtained with a different crystal of the same ingot in a preliminary investigation of the [001] projection, using data obtained with Weissenberg photographs.

The refinement was carried out, firstly by least-squares, and subsequently based on difference Fourier syntheses. The R-factors for the ordered, totally disordered and observed structures are listed in Table I. Figures 1 to 4 show the Fourier maps (direct and difference) for the three ordering arrangements tested.

Fig. 1 (next page) — F_o Fourier sections for the observed structure. Contours are at arbitrary equal intervals. Dashed lines represent negative contours. A), B) and C) show sections at $c = 0$, $c = 0.25$, $c = 0.5$ respectively.

Fig. 2 (next page) — $(F_o - F_c)$ Fourier sections for the observed structure. Countours are at 1/10 those of F_o in fig. 1. Dots mark the atomic sites. A), B) and C) as in fig. 1.

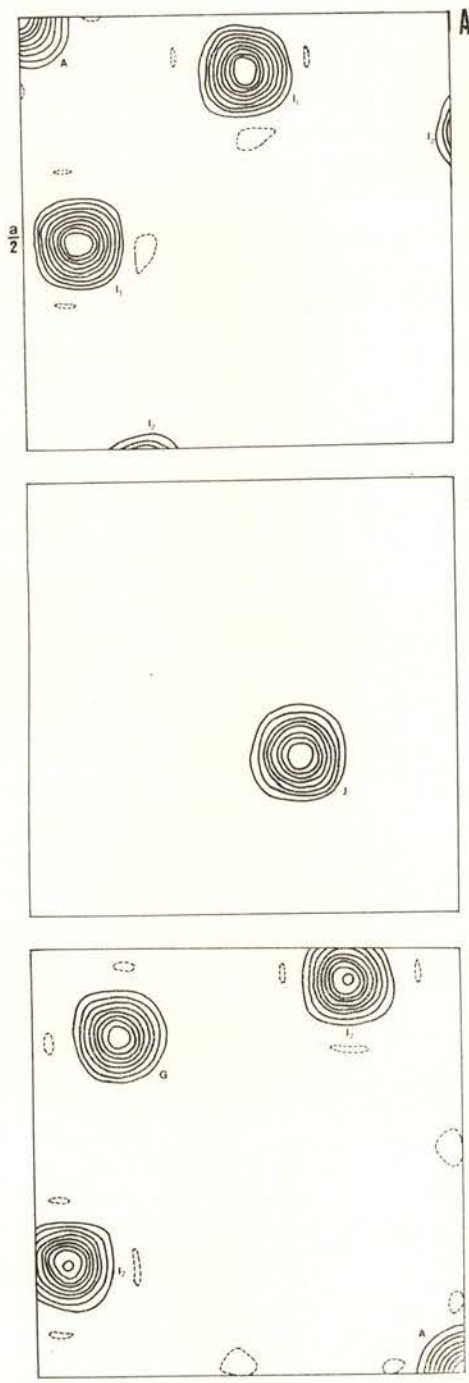

Fig. 1

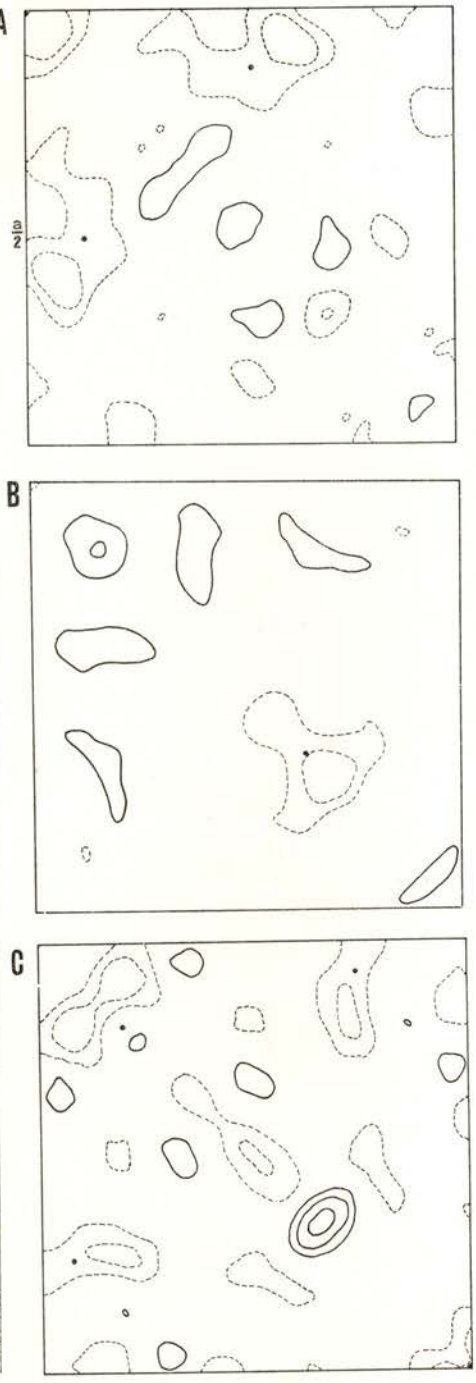

Fig. 2

V and Co (Z = 23 and Z = 27) are very close in the periodic table which is a disadvantage for the study of the ordering by an X-ray technique. However, the method used by Alte da Veiga et al. [1] for the estimation of the errors (Fig. 5) shows that the ordering observed departs significantly from complete ordering.

TABLE I — Atomic parameters and possible ordering arrangements in σ-VCo

Type	Site	Parameter	Occupancy (No. At. Co)		
			Ordered	Disordered	Observed
2 (a) (0, 0, 0)	A	—	2	0.76	1.3
8 (i) (x_1, y_1, 0)	I_1	$x_1 = 0.0664$ $y_1 = 0.2616$	8	3.04	6.8
8 (i) (x_2, y_2, 0)	I_2	$x_2 = 0.5369$ $y_2 = 0.1310$	0	3.04	1.25
4 (g) (x_3, $\bar{x}_3$, 0)	G	$x_3 = 0.4001$	0	1.52	0.05
8 (j) (x_4, x_4, z_4)	J	$x_4 = 0.3176$ $z_4 = 0.2479$	0	3.04	2.0
R-factors			7.88	9.04	6.86

4 — DISCUSSION

The ordering of the σ-phases has been discussed in terms of two factors: electronic and size of the constituent atoms. In the σ-phase of the sistem (V, Co) both factors are cooperative and it would be expected that, owing to its almost stoichiometric

Fig. 3 (next page) — ($F_o - F_c$) Fourier sections for the ordered structure. Contours are at 1/10 those of F_o in fig. 1. A), B) and C) as in fig. 1.

Fig. 4 (next page) — ($F_o - F_c$) Fourier sections for the totally disordered structure. Contours are at 1/10 those of F_o in fig. 1. A), B) and C) as in fig. 1.

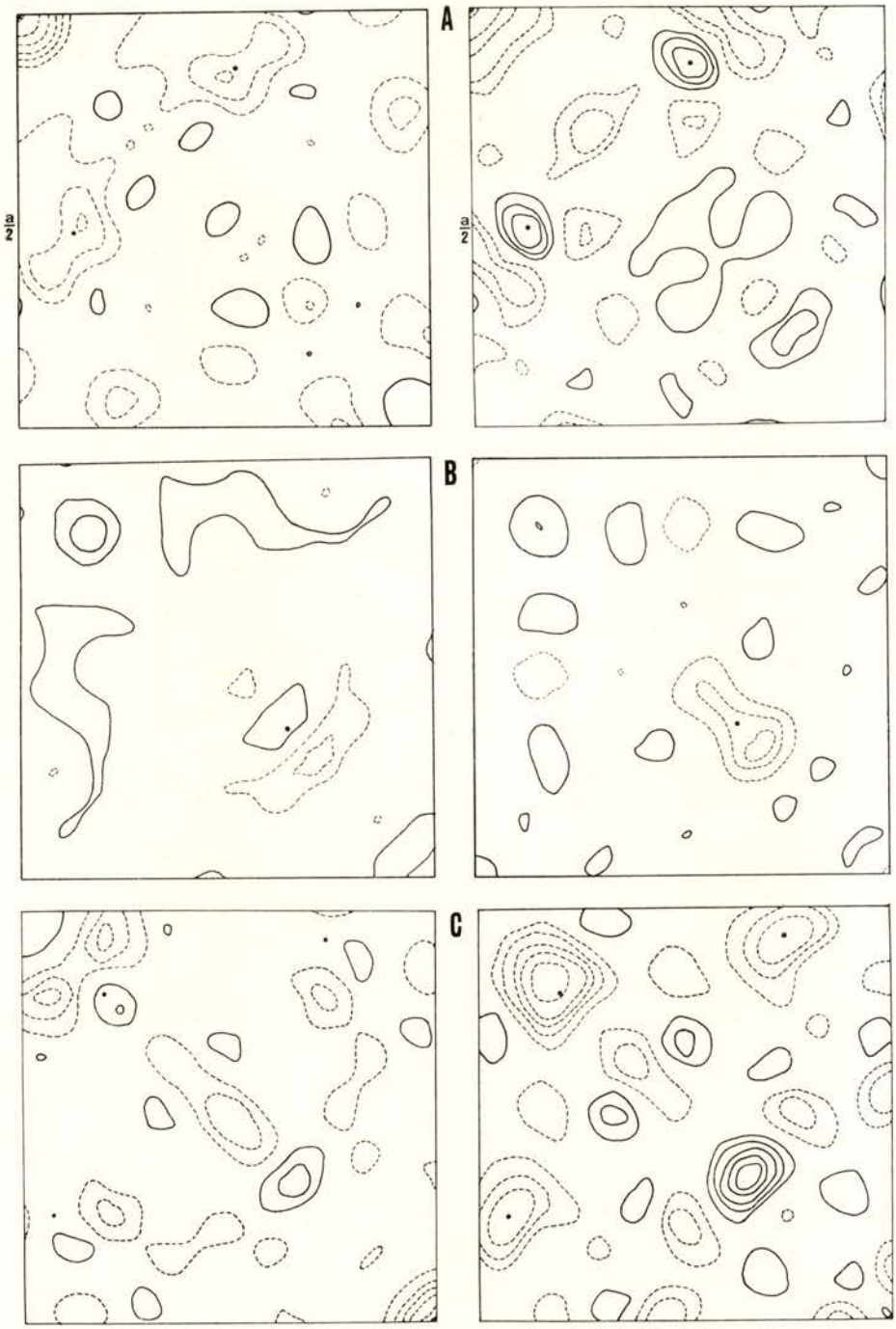

Fig. 3

Fig. 4

composition, the structure would be completely ordered; however, this is not observed. No attempt to interpret this result is made until the study of the ordering in a phase with a different composition is completed. The dependence of ordering on composition will be studied in order to investigate preferential occupation of the atomic sites as observed in the σ-phases Cr_2Ru and Cr_2Os [1].

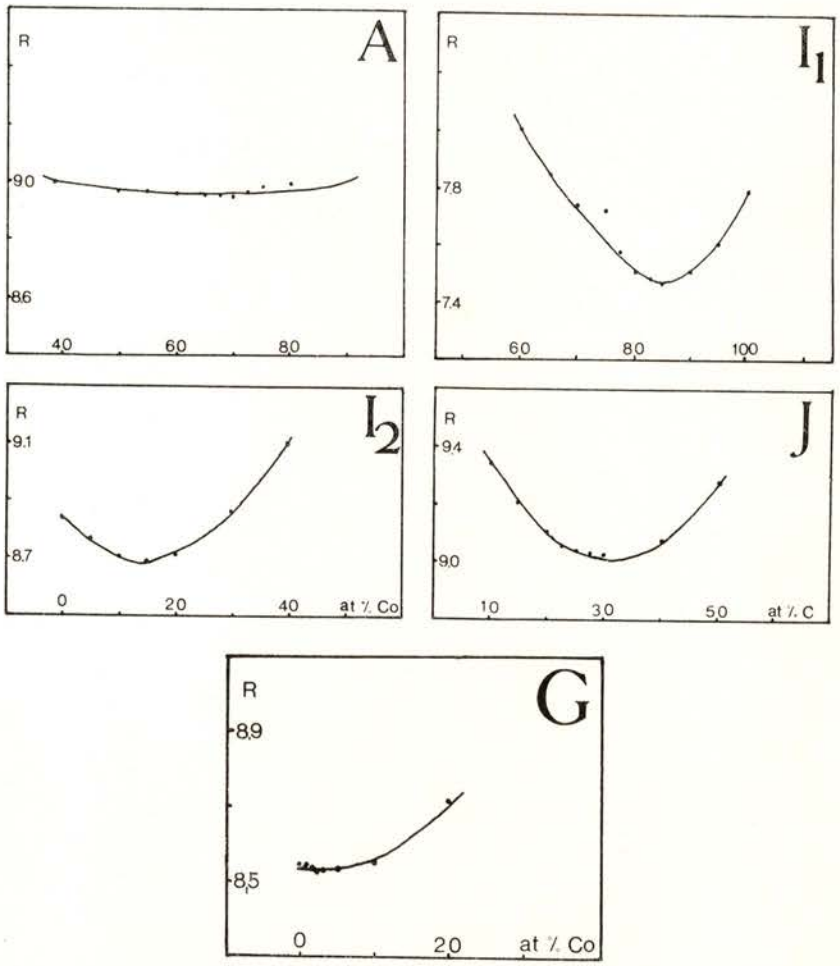

Fig. 5 — Plot of the R-factors against occupancies for each atomic site. Whilst the occupancy for each atomic site was varied, all the remaining sites were assumed to be occupied by the same type of «compound» atom, as required by the composition of the alloy.

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