THE ORDERING OF THE σ-PHASE Cr_2Ru

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The σ-phase structure of Cr_2Ru has been confirmed by single crystal measurements. Six out of seven parameters have been refined. The distribution of atoms in the available sites appears to be disordered; the ratio of the two atoms is almost the same in the different sites.

1. *INTRODUCTION*

The sigma phases and related structures have been previously investigated by the present author. The structures of the phases μ-Mo_6Co_7 and σ-Mo_3Co_2 have already been refined (FORSYTH and ALTE DA VEIGA, 1962 and 1963) and a comparative study of the sigma phases with those having the $A15$ type of structure (β-W structure) has also been undertaken (ALTE DA VEIGA, 1963). It appeared from this study that it was likely that the phase σ-Cr_2Ru would be completely ordered, like σ-Nb_2Al (BROWN and FORSYTH, 1961), with the larger atom, Ru, occupying the two 12-coordinated sites and Cr the two 14-coordinated and the 15-coordinated sites.

WATERSTRAT and KASPER (1957) have determined, from powder work, that the structure of σ-Cr_2Ru was disordered, and stated that their measurements were not accurate enough to detect small amounts of ordering. As our experience in the refinement of σ-Mo_3Co_2 had shown that the low angle reflections were also sensitive to small

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adjustments of the atomic parameters, we have decided to undertake both the determination of the ordering of σ-Cr_2Ru and the refinement of the structure using the single crystal technique.

2. *MATERIAL, UNIT CELL AND SPACE GROUP*

The phase Cr_2Ru is homogeneous over about 2 at. % in the region of 66 at. % *Cr*; $a = 9.007$ and 9.03, $c = 4.6630$ and 4.671 Å (PEARSON, 1958, p. 558). The ingot of σ-Cr_2Ru was kindly supplied by Dr. M. Nevitt, Argonne National Laboratory, Illinois, U. S. A.. A great difficulty was experienced in findind a single crystal.

Laue, oscillation and Weissenberg photographs were consistent with the space groups $P4_2nm$, $P\bar{4}n2$ and $P4_2/mnm$. The subsequent refinement of the structure has justified the choice of the last space group.

3. *REFINEMENT OF THE STRUCTURE*

Our main purpose was the investigation of the ordering and this can be well determined from reflections from the zero layer of the [001] projection. This projection also allows the refinement of six out of seven atomic parameters. The reflections were collected using normal-beam Weissenberg photographs; filtered $MoK\alpha$ radiation and a multiple-film technique were used. The reflections were measured by visual comparison with an intensity scale obtained using the 410 reflection from the same crystal. The intensities were corrected for Lorentz and polarization factors and allowance was made for resolution of the $\alpha_1\alpha_2$ doublet by scalling F_o and F_c in regions of $\sin\theta/\lambda$; this method of scaling also makes adequate allowance for the variation of absorption in the crystal used.

The structure was refined using $(F_o - F_c)$ syntheses. The atomic scattering factors were generated from the analytical constants for Cr^{2+} and *Ru* proposed by FORSYTH and WELLS (1959).

The refinement was started with an ordered arrangement of atoms, *Ru* in *A* and I_1 sites and *Mo* in I_2, *G* and *J*, using the σ-Mo_3Co_2 parameters (FORSYTH and ALTE DA VEIGA, 1963), shown in table 1; the corresponding initial *R*-factor was 0.48. A completely disordered arrangement (i. e. one in which all the sites are occupied by the two atoms in the same ratio) was then tried and the corresponding initial

R-factor was 0.24. The final *R*-factors obtained for reflections out to $\sin\theta/\lambda = 0.99\ \text{Å}^{-1}$ were 0.076 for the arrangement shown in table 2 and 0.092 for a completely disordered arrangement.

The final F_o and $(F_o - F_c)$ syntheses corresponding to the arrangement which gave lowest *R*-factor are shown in fig. 1. The $(F_o - F_c)$ Fourier synthesis corresponding to a completely disordered arrangement but using the final atomic parameters is shown in fig. 2.

There was no evidence that even the strongest reflections are afected by extinction. The final parameters are listed in table 1. The standard deviations were estimated from the final F_o and $(F_o - F_c)$ Fourier syntheses by the method suggested by LIPSON and COCHRAN (1953).

Values of SF_o and F_c are listed in table 3.

4. *DISCUSSION*

It is our intention to complete the refinement of the structure of σ-Cr_2Ru and determine accurately the unit cell dimensions, but the results obtained so far are the relevant ones.

Table 2 shows that the structure appears to be almost completely disordered. It may possibly be argued that there is a slight trend to an ordering, as table 2 and figs. 1 and 2 show that both the *R*-factor and the difference map are slightly better for that arrangement than for a complete disordering. The same conclusion may possibly be better reached if the calculated structure factors for a complete disordering, but using the final atomic parameters, are compared with those (listed in table 3) which give the lowest *R*-factor. The comparison is made in table 4 only for the calculated structure factors which are in worst agreement with the observed ones.

The trend to an ordering is shown by an increase of the *A*-transition metal, *Cr*, in the *J* site and a decrease in the I_2 site, which is surprising because the two sites are similar. They both are 14-coordinated and the *J* sites are those which form rows of sites ...*JJJJ*... between which the distances are very short, while the I_2 sites form rows GI_2I_2G and between these sites the distances are also short, mainly $I_2 - I_2$ (FORSYTH and ALTE DA VEIGA, 1963; ALTE DA VEIGA, 1963).

In the comparative study of the σ-phases and structures of the *A*15 type (ALTE DA VEIGA, 1963) we had assumed that all these were

ordered as they exist only at a stoichiometric composition. In the case of (*Cr,Ru*) alloys, the cell dimensions of Cr_3Ru (which has an *A*15 type of structure) and σ-Cr_2Ru have suggested, under the assumption that Cr_3Ru is completely ordered, that the *J* sites of σ-Cr_2Ru would be completely occupied by *Cr;* this is in some agreement with the trend of the *Cr* atoms to occupy the *J* site (see table 2). It is certainly of interest to determine the ordering of Cr_3Ru; this work is being undertaken in our laboratory.

It has been mentioned above that we had noticed that the low angle reflections were also sensitive to small adjustments of the atomic parameters. For the reflections out to sin $\theta/\lambda = 0.99$ $\mathring{A}^{-1}$ an *R*-factor of 0.23 was obtained from structure factors calculated for the arrangement which gave the lowest *R*-factor (0.076), but using the initial atomic parameters. This corresponds to a determination of the ordering without refining the atomic parameters. The *R*-factors for the different ranges of sin θ/λ are compared in table 5; they clearly show how sensitive the low angle reflections are to small adjustements of the atomic parameters. The determination of an ordering which is done without refining the structure is likely to lead to less precise results even if only the low angle reflections are used.

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TABLE 1

Atomic parameters and their standard deviations in σ-Mo_3Co_2 and σ-Cr_2Ru

Type	Site	σ-Mo_3Co_2	σ-Cr_2Ru
2 (*a*) (0,0,0)	*A*		
8 (*i*) (x_1, y_1, 0)	I_1	$x_1 = 0.0670 \pm 0.0003$	0.0643 ± 0.0003
		$y_1 = 0.2550 \pm 0.0003$	0.2585 ± 0.0003
8 (*i*) (x_2, y_2, 0)	I_2	$x_2 = 0.5365 \pm 0.0002$	0.5365 ± 0.0002
		$y_2 = 0.1283 \pm 0.0002$	0.1338 ± 0.0002
4 (*g*) (x_3, $\bar{x}_3$, 0)	*G*	$x_3 = 0.3973 \pm 0.0002$	0.4007 ± 0.0003
8 (*j*) (x_4, x_4, z_4)	*J*	$x_4 = 0.3180 \pm 0.0001$	0.3159 ± 0.0001
		$z_4 = 0.2500 \pm 0.0001$	—

TABLE 2

Possible ordering arrangements in σ-Cr_2Ru. The last column shows the arrangement which gives lowest *R*-factor

Site	Atom	Ordered	Completely disordered	Ordering determined
A	*Ru*	2	0.667	0.5
	Cr	0	1.333	1.5
I_1	*Ru*	8	2.667	2.8
	Cr	0	5.333	5.2
I_2	*Ru*	0	2.667	3.2
	Cr	8	5.333	4.8
G	*Ru*	0	1.333	1.5
	Cr	4	2.667	2.5
J	*Ru*	0	2.667	2
	Cr	8	5.333	6
R-factor			0.092	0.076

TABLE 3

Observed and calculated structure amplitudes of *hk*0 reflections from σ-Cr_2Ru

sin θ/λ	h	k	F^c	SF_o	h	k	F_c	SF_o
0 — 0.29	0	0	873	—	2	3	— 14	17
	1	1	— 1	—	3	3	289	275
	0	2	5	8	1	4	— 308	291
	1	2	— 11	12	2	4	3	7
	2	2	— 17	19	3	4	11	12
	1	3	— 6	8	1	5	17	19
0.29 — 0.40	4	4	— 14	19	1	6	— 12	8
	2	5	7	9	2	6	— 23	29
	3	5	— 9	11	4	6	16	19
	4	5	11	14	1	7	— 29	29
	5	5	182	172	2	7	210	206
0.40 — 0.51	5	6	— 41	43	0	8	— 18	24
	6	6	166	159	2	8	189	178
	3	7	6	12	4	8	8	11
	4	7	— 6	15	1	9	15	13
	6	7	23	27	2	9	— 26	28
0.51 — 0.60	5	8	37	33	0	10	— 14	14
	6	8	— 29	31	1	10	— 26	31
	3	9	5	9	2	10	— 10	12
	5	9	— 42	40	3	10	12	14
	6	9	— 135	127	4	10	— 24	25
0.60 — 0.68	7	9	32	32	2	11	23	20
	8	9	— 37	33	3	11	— 39	39
	5	10	116	115	5	11	— 27	29
	6	10	39	38	0	12	10	11
	7	10	— 24	22	1	12	39	56
	1	11	135	129	3	12	— 111	107
0.68 — 0.78	9	9	80	78	6	12	— 21	19
	8	10	— 12	11	7	12	25	25
	9	10	46	44	3	13	23	27
	10	10	100	98	4	13	— 40	37
	8	11	28	28	5	13	— 22	25
	9	11	— 12	15	0	14	— 57	52
	4	12	19	17	2	14	18	22
	5	12	— 19	19				

sin θ/λ	h	k	F_c	SF_o	h	k	F_c	SF_o
0.78 — 0.89	10	11	— 24	26	3	14	— 20	20
	11	11	20	26	4	14	90	97
	8	12	— 32	30	5	14	20	10
	9	12	— 15	18	6	14	— 13	15
	10	12	35	34	7	14	— 30	34
	6	13	35	32	2	15	— 29	30
	7	13	66	62	3	15	— 15	15
	8	13	65	63	4	15	58	54
	9	13	37	34	0	16	59	58
0.89 — 0.99	11	12	— 21	19	9	15	— 15	16
	12	12	52	56	2	16	— 18	19
	11	13	— 37	33	3	16	23	19
	12	13	34	35	4	16	71	70
	8	14	47	46	6	16	18	16
	10	14	— 29	23	8	16	— 43	46
	11	14	— 41	42	3	17	— 26	30
	6	15	— 9	16	4	17	— 43	43
	7	15	31	32	5	17	34	33

TABLE 4

a) Arrangement which gives lowest *R*-factor.
b) Complete disordering.

sin θ/λ	h	k	*a*)		*b*)	
			F_c	SF_o	F_c	SF_o
0.123	1	2	— 11	12	1	12
0.156	2	2	— 17	19	— 5	19
0.296	2	5	7	9	— 2	9
0.550	0	10	— 14	14	— 3	15

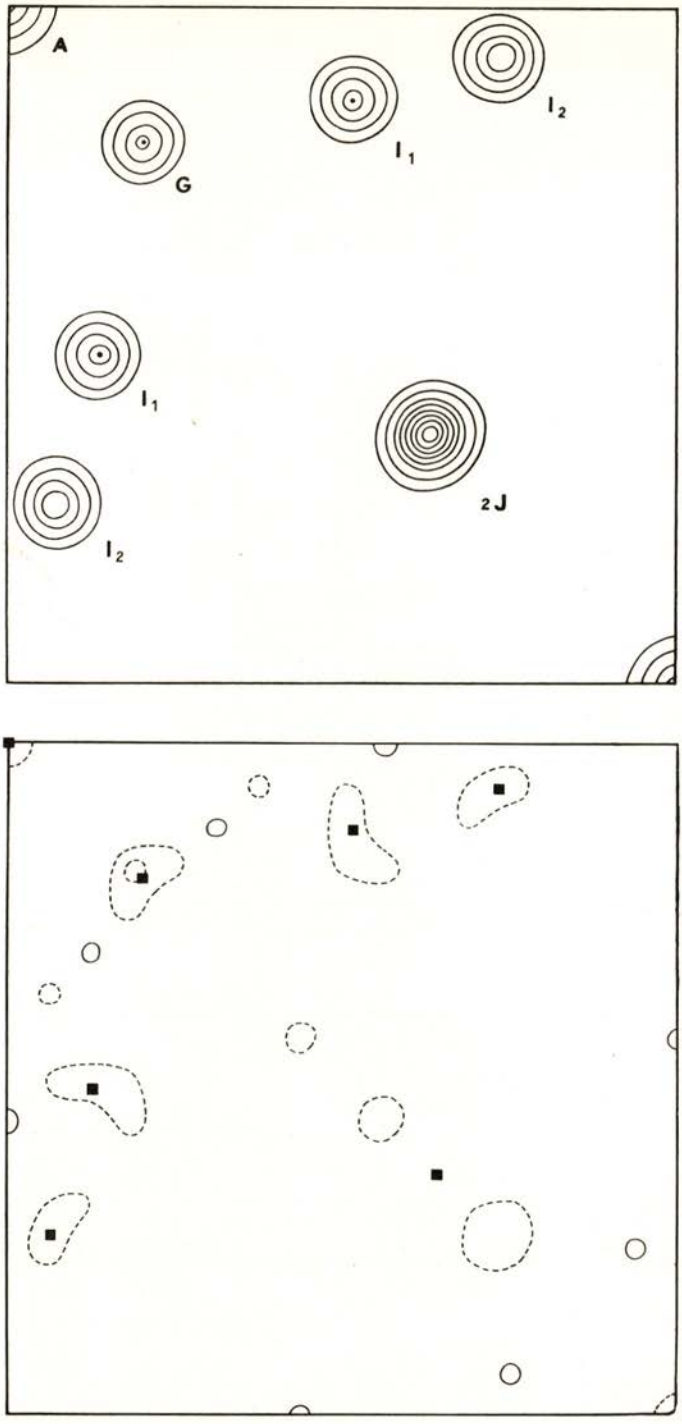

Fig. 1 — Final F_o and $(F_o - F_c)$ [001] Fourier projections.

a) F_o. The contours are at equal arbitrary intervals.

b) $(F_o - F_c)$. The contour intervals are one-tenth those of the F_o; negative contours are shown as broken lines. Squares mark the atomic sites.

TABLE 5

a) Final *R*-factors for the different ranges of sin θ/λ.

b) *R*-factors from structure factors calculated using the final ordering, the same as in *a*), but the initial atomic parameters.

sin θ/λ	*R* — factors	
	a)	*b*)
0 — 0.29	0.069	0.146
0.29 — 0.40	0.074	0.168
0.40 — 0.51	0.104	0.200
0.51 — 0.60	0.087	0.254
0.60 — 0.68	0.066	0.115
0.68 — 0.78	0.061	0.443
0.78 — 0.89	0.082	0.225
0.89 — 0.99	0.076	0.227

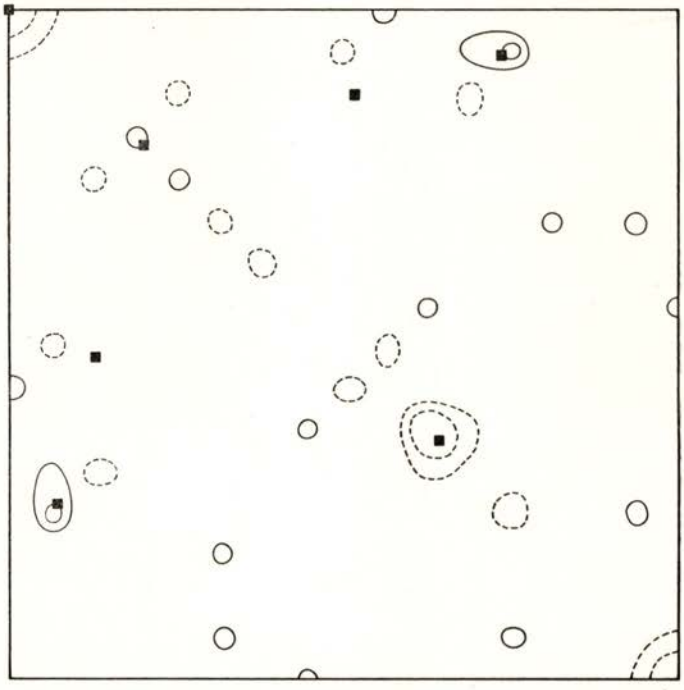

Fig. 2 — $(F_o - F_c)$ [001] Fourier projection assuming that all the sites are occupied by the two atoms in the same ratio. The atomic parameters are the same as those used for the Fourier projections shown in fig. 1.

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