ACTA CHEMICA SCANDINAVICA 23 (1969) 1191–1199

Crystal Structure Refinement of Cr_3C_2

STIG RUNDQVIST and GUNILLA RUNNSJÖ

Institute of Chemistry, University of Uppsala, Uppsala, Sweden

The crystal structure of Cr_3C_2 has been refined from single crystal X-ray diffraction data obtained both by photographic methods and counter methods. The results are compared with those reported in earlier investigations, and the structural relationships between Cr_3C_2 and other compounds are discussed.

The first X-ray crystallographic examination of the Cr_3C_2 structure was made by Westgren and Phragmén.[1] They found that the unit cell is orthorhombic and contains four formula units. Later, Hellbom and Westgren [2] (H and W) presented a structure proposal based on qualitative intensity estimations from single crystal rotation photographs and from powder photographs. The space group was reported to be *Pbnm* with three sets of chromium atoms and two sets of carbon atoms occupying fourfold positions in the mirror planes. The positions of the chromium atoms were obtained by a systematic variation of the six positional parameters, until a satisfactory agreement between calculated and observed intensities was reached. Assuming a radius of about 1.3 Å for the chromium atoms, H and W found that there were twelve interstices, each capable of accomodating an atom with a radius of about 0.8 Å, between the chromium atoms in each unit cell. A carbon atom located at the centre of one of these interstices would have a triangular prismatic environment of six chromium atoms. The centres of the twelve interstices correspond to three sets of fourfold positions in space group *Pbnm*. Since there are only eight carbon atoms in the unit cell, three combinations of two fourfold sets were possible (disregarding the possibility of a random distribution of the eight carbon atoms in all twelve interstices). A decision between the three alternatives on the basis of intensity calculations was not possible on account of the low scattering power of carbon and the qualitative character of the observed intensity material. H and W suggested the most probable alternative to be an arrangement involving infinite zig-zag chains of carbon atoms. They were led to this proposal by assuming a structural analogy between Cr_3C_2 and FeB. In the FeB structure, which was determined by Bjurström [3] at the same time as H and W were engaged in their Cr_3C_2 studies, the boron atoms are bonded in infinite chains.

A re-examination of the Cr_3C_2 structure by neutron powder diffraction methods was made by Meinhardt and Krisement.[4] They found that the carbon arrangement as proposed by H and W was incorrect. Of the two remaining combinations of two fourfold carbon positions, that involving carbon atoms located as far as possible from each other was found to give satisfactory agreement between observed and calculated intensities. The positional parameters for the carbon atoms were varied until the best agreement between observed and calculated intensities was reached, but no attempt was made to improve the chromium parameters given by H and W.

In a series of crystal-chemical studies of compounds between transition metals and elements with unfilled *p* levels currently being carried out at this Institute, the conditions governing the coordination of the metal atoms about the *p* element atoms have received considerable attention (see, *e.g.*, Refs. 5, 6). Recently, a structure determination of Hf_3P_2 by Lundström [7] showed that the atomic arrangement in this compound is very closely related to that in Cr_3C_2. In this connection it appeared desirable to obtain more accurate structural information on Cr_3C_2. The present paper presents the results of a least-squares refinement of the Cr_3C_2 structure from single crystal X-ray diffraction data.

EXPERIMENTAL

Preparation. Cr_3C_2 was prepared by melting mixtures of chromium (Gesellschaft für Elektrometallurgie mbH, Werk Nuremberg, purity 99.97 %) and graphite powder in an arc furnace under purified argon. Well developed single crystals were obtained directly from the melts.

X-Ray work. Powder diffraction patterns were recorded in Guinier-Hägg type focussing cameras using strictly monochromatic Cr$K\alpha_1$ radiation and silicon ($a = 5.43054$ Å) as the internal calibration standard. Single crystal diffraction films were recorded in Zr-filtered MoK radiation with an ordinary Weissenberg camera employing the equi-inclination method. The multiple-film technique was used and the intensities were estimated visually by comparison with an intensity scale obtained from timed exposures of one reflexion from the crystal. The intensities used in the final refinement were measured with a General Electric manual single crystal orienter, using Zr-filtered MoK radiation and a scintillation counter. The $2\theta - \theta$ scan technique was employed to obtain the integrated intensities, and background corrections were made in the usual manner. The stability of the instrument was checked frequently by measurements of a control reflexion. The intensities of the $h0l$, $h1l$ and $hk0$ reflexions were measured within the range $0° < 2\theta < 140°$.

Calculations. All calculations were made on a CDC 3600 computer using programs listed in Table 1.

THE STRUCTURE DETERMINATION

A preliminary examination of the single crystal Weissenberg films confirmed the results of H and W as regards the diffraction symmetry and the unit cell dimensions. More accurate cell dimensions were obtained by least-squares refinements of powder diffraction data. (There is probably a misprint in Ref. 2, where the shortest axis is reported to be 2.281 kX instead of 2.821 kX.)

Using the $F(h0l)$ and $F(h1l)$ values obtained from the photographic intensity material, the electron density section $\varrho(x\,0.25\,z)$ was calculated. The signs of the structure factors were based on the chromium contributions only,

Table 1. Computer programs used for the crystallographic calculations on the CDC 3600 computer in Uppsala (program 2, written in ALGOL, the remaining in FORTRAN IV).

Program performing	Authors
1. Least squares refinement of unit cell dimensions.	J. Tegenfeldt, Uppsala, Sweden.
2. Calculation of setting angles for General Electric's Manual and Automatic Single Crystal Orienters.	R. Norrestam, Stockholm, Sweden.
3. Lorentz-polarisation, absorption and extinction corrections.	P. Coppens, L. Leiserowitz and D. Rabinovich, Rehovoth, Israel; modified by O. Olofsson and M. Elfström, Uppsala and (incorporation of extinction correction) by B. Brandt and S. Åsbrink, Stockholm, Sweden.
4. Least squares refinement of positional parameters and temperature factors.	P. K. Gantzel, R. A. Sparks and K. N. Trueblood, Los Angeles, U.S.A.; modified by A. Zalkin, Berkeley, U.S.A. and by C.-I. Brändén, R. Liminga and J.-O. Lundgren, Uppsala, Sweden.
5. Fourier summations and structure factor calculations.	A. Zalkin, Berkeley, U.S.A.; modified by R. Liminga and J.-O. Lundgren, Uppsala, Sweden.
6. Interatomic distances.	A. Zalkin, Berkeley, U.S.A.

assuming that the chromium atoms occupy three sets of 4*c* positions in space group *Pnma* with the parameter values as reported by H and W. The electron density section contained maxima at the expected chromium positions, and in addition, smaller maxima appeared at positions corresponding to the carbon sites as proposed by Meinhardt and Krisement.[4] The atomic positions and individual isotropic temperature factors were further refined by the least-squares method. The observed structure factor values were corrected for absorption, the absorption coefficient being calculated from values taken in Ref. 8. Weights were assigned according to the formula $w=1/(a+|F_o|+c|F_o|^2)$. The final values chosen for a and c were 16 and 0.021, respectively. Atomic scattering factors were interpolated from tables given in Ref. 8. After some cycles of refinement it was observed that the intensity material suffered from extinction effects. The strongest reflexions were then excluded, and the refinement was continued until the parameter shifts were negligible. The final R-value for the 474 remaining reflexions was 0.13. This value is rather high, and a comparison of the calculated and observed structure factors indicated that extinction effects still affected the remaining stronger reflexions. Since extinction errors generally have a rather small influence on the positional parameters, and since a more accurate intensity material obtained by counter methods was available, no further improvements were considered worthwhile. The final parameters obtained by the photographic method are given in Table 2.

A second set of intensities for Cr_3C_2 was measured by means of a scintillation counter on the General Electric single crystal orienter. The crystal used was needle-shaped with the needle axis coinciding with the shortest crystallographic axis. The crystal was bounded by well developed {001} and {101}

Table 2. Final structure data for Cr_3C_2.

Space group $Pnma$, $Z=4$.
$a = 5.5329$ Å, $\sigma(a) = 0.0005$ Å
$b = 2.8290$ Å, $\sigma(b) = 0.0002$ Å
$c = 11.4719$ Å, $\sigma(c) = 0.0007$ Å
All atoms are situated in 4c positions.

Parameter values obtained from intensities recorded photographically.

Atom	x	$\sigma(x)$	z	$\sigma(z)$	B (Å^2)	$\sigma(B)$
Cr1	0.0157	0.0004	0.4015	0.0002	0.16	0.02
Cr2	0.1808	0.0004	0.7737	0.0002	0.14	0.02
Cr3	0.8691	0.0003	0.9312	0.0002	0.12	0.02
C1	0.1008	0.0024	0.2055	0.0011	0.29	0.12
C2	0.2432	0.0021	0.9536	0.0010	0.17	0.11

Parameter values obtained from intensities measured with scintillation counter.

Atom	x	$\sigma(x)$	z	$\sigma(z)$	B (Å^2)	$\sigma(B)$
Cr1	0.01632	0.00018	0.40165	0.00009	0.539	0.012
Cr2	0.18079	0.00018	0.77351	0.00009	0.529	0.012
Cr3	0.86913	0.00018	0.93131	0.00009	0.505	0.012
C1	0.0993	0.0013	0.2061	0.0006	0.82	0.07
C2	0.2404	0.0013	0.9531	0.0006	0.83	0.08

planes, the largest and shortest cross-sections being 0.07 and 0.05 mm, respectively. The length of the needle was about 0.23 mm, and the somewhat irregular end sections could be fairly well approximated by (010) planes.

The intensities for the ($h0l$), ($\bar{h}1l$), and ($hk0$) reflexions were measured. Of the 716 accessible reflexions, 485 had measurable intensities. F_o values were obtained from the intensities by applying the usual angular factors and a correction for absorption. A comparison of the calculated structure factors obtained in the refinement of the photographic intensity material with the structure factors measured on the single crystal orienter indicated that the latter were also affected by extinction. After removing the 29 largest F_o values, the remaining 456 reflexions were used in a preliminary least-squares refinement. At the end of this refinement, the R-value was 0.067. An extinction correction was then applied using Zachariasen's method,[9] and some further cycles of refinement yielded a final R-value of 0.068 for the 485 reflexions observed. A weighting scheme based solely on counter statistics was found to be less satisfactory, and therefore the weighting formula mentioned previously was used with $a=10$ and $c=0.040$.

Finally, the possibility that Cr_3C_2 has the lower space group symmetry $Pn2_1a$ was investigated. In space group $Pn2_1a$, the atoms would occupy 4a positions with free y parameters. A least-squares refinement was made assuming $Pn2_1a$ symmetry. The y parameter for one of the chromium atoms was held fixed at 0.25, the initial y parameter for a second chromium position was shifted from 0.25 to 0.23, and the initial y parameters for the remaining atoms were put equal to 0.25. The refinement converged to an R-value of 0.067.

Table 3. Observed and calculated structure factors for Cr_3C_2. ($F_o = 0.0$ for reflexions too weak to be measured).

h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$
0	0	2	0.0	1.5	4	0	15	15.0	14.2	8	0	25	0.0	1.0	1	1	2	87.8	104.4	5	1	5	11.3	11.2
0	0	4	0.0	4.6	4	0	16	33.4	30.6	9	0	1	0.0	1.6	1	1	3	31.3	34.7	5	1	6	0.0	2.4
0	0	6	161.4	147.1	4	0	17	28.7	25.6	9	0	2	0.0	0.6	1	1	4	66.7	74.1	5	1	7	7.1	6.9
0	0	8	29.8	27.8	4	0	18	0.0	0.2	9	0	3	11.9	10.7	1	1	5	65.5	71.2	5	1	8	43.7	44.3
0	0	10	23.4	20.8	4	0	19	7.0	7.4	9	0	4	0.0	0.4	1	1	6	0.0	1.8	5	1	9	44.9	45.8
0	0	12	14.5	12.8	4	0	20	26.0	28.8	9	0	5	0.0	0.1	1	1	7	7.7	8.2	5	1	10	34.1	34.7
0	0	14	22.4	22.0	4	0	21	10.8	12.1	9	0	6	19.4	23.0	1	1	8	64.2	69.4	5	1	11	0.0	0.5
0	0	16	21.3	19.9	4	0	22	20.9	21.4	9	0	7	0.0	4.3	1	1	9	55.0	51.8	5	1	12	11.9	11.7
0	0	18	26.4	23.8	4	0	23	17.2	17.5	9	0	8	0.0	3.3	1	1	10	14.0	13.4	5	1	13	0.0	2.0
0	0	20	9.8	8.7	4	0	24	0.0	2.1	9	0	9	22.7	24.8	1	1	11	43.4	40.4	5	1	14	28.6	27.7
0	0	22	8.9	7.5	4	0	25	0.0	5.6	9	0	10	0.0	1.8	1	1	12	0.0	4.3	5	1	15	34.8	34.0
0	0	24	0.0	26.0	4	0	26	11.6	11.5	9	0	11	0.0	1.7	1	1	13	0.0	3.8	5	1	16	23.8	22.4
0	0	26	0.0	0.2	4	0	27	4.3	4.3	9	0	12	0.0	33.9	1	1	14	26.5	26.0	5	1	17	0.0	6.1
0	0	28	0.0	3.5	4	0	28	7.7	7.3	9	0	13	0.0	4.4	1	1	15	33.1	32.6	5	1	18	22.7	20.2
0	0	30	0.0	17.0	4	0	29	0.0	5.5	9	0	14	0.0	0.1	1	1	16	11.8	10.7	5	1	19	0.0	5.0
1	0	1	7.5	5.7	5	0	1	47.0	43.6	9	0	15	22.7	22.2	1	1	17	0.0	3.6	5	1	20	7.7	9.6
1	0	2	0.0	11.7	5	0	2	43.2	39.2	9	0	16	4.2	5.3	1	1	18	0.0	0.4	5	1	21	18.2	15.4
1	0	3	13.1	12.9	5	0	3	0.0	4.7	9	0	17	0.0	0.2	1	1	19	0.0	1.4	5	1	22	7.3	8.5
1	0	4	60.6	64.2	5	0	4	61.6	58.2	9	0	18	0.0	25.1	1	1	20	0.0	2.2	5	1	23	7.5	8.9
1	0	5	70.4	69.3	5	0	5	56.1	56.3	9	0	19	0.0	2.2	1	1	21	10.3	12.0	5	1	24	14.9	15.7
1	0	6	20.6	19.9	5	0	6	0.0	4.2	9	0	20	6.8	6.9	1	1	22	10.3	11.6	5	1	25	6.0	6.5
1	0	7	42.0	43.3	5	0	7	9.8	10.0	9	0	21	10.6	9.3	1	1	23	12.8	14.0	5	1	26	0.0	1.3
1	0	8	26.7	26.3	5	0	8	0.0	3.0	9	0	22	7.0	7.2	1	1	24	0.0	5.2	5	1	27	0.0	3.1
1	0	9	36.5	34.5	5	0	9	10.0	12.4	9	0	23	0.0	4.0	1	1	25	0.0	1.5	6	1	0	64.6	62.4
1	0	10	65.8	63.3	5	0	10	36.1	37.1	10	0	0	8.3	9.0	1	1	26	14.2	15.0	6	1	1	16.5	17.0
1	0	11	49.7	46.9	5	0	11	43.1	42.1	10	0	1	27.7	30.3	1	1	27	0.0	2.0	6	1	2	13.6	14.1
1	0	12	8.6	7.1	5	0	12	0.0	4.7	10	0	2	9.3	10.7	1	1	28	6.9	8.0	6	1	3	46.0	46.1
1	0	13	34.6	31.9	5	0	13	12.8	11.8	10	0	3	13.6	13.9	1	1	29	14.8	13.9	6	1	4	5.6	5.8
1	0	14	28.8	27.2	5	0	14	11.3	10.4	10	0	4	0.0	0.5	2	1	0	16.7	10.2	6	1	5	18.6	18.6
1	0	15	39.3	36.7	5	0	15	11.2	10.4	10	0	5	28.0	23.6	2	1	1	79.9	84.9	6	1	6	45.4	45.6
1	0	16	35.8	32.4	5	0	16	11.8	10.0	10	0	6	0.0	5.0	2	1	2	28.3	28.6	6	1	7	7.0	6.7
1	0	17	23.1	20.6	5	0	17	11.9	13.9	10	0	7	18.0	19.1	2	1	3	23.6	30.4	6	1	8	15.2	15.3
1	0	18	11.5	9.5	5	0	18	0.0	0.3	10	0	8	14.2	9.2	2	1	4	36.8	39.7	6	1	9	10.6	10.2
1	0	19	20.8	17.8	5	0	19	10.4	12.0	10	0	9	14.8	15.0	2	1	5	36.7	39.7	6	1	10	0.0	0.1
1	0	20	13.3	14.9	5	0	20	8.0	6.3	10	0	10	12.3	12.3	2	1	6	10.0	10.1	6	1	11	10.4	9.6
1	0	21	23.6	26.3	5	0	21	0.0	1.6	10	0	11	9.4	6.3	2	1	7	44.5	49.8	6	1	12	13.5	13.2
1	0	22	0.0	1.3	5	0	22	0.0	5.8	10	0	12	0.0	0.7	2	1	8	48.7	49.7	6	1	13	25.7	25.3
1	0	23	0.0	0.1	5	0	23	10.1	10.0	10	0	13	0.0	0.5	2	1	9	20.0	19.5	6	1	14	14.5	13.4
1	0	24	15.3	15.3	5	0	24	0.0	5.1	10	0	14	0.0	5.0	2	1	10	22.5	22.4	6	1	15	10.5	11.5
1	0	25	7.4	7.9	5	0	25	0.0	4.9	10	0	15	11.3	11.0	2	1	11	16.1	15.5	6	1	16	0.0	0.7
1	0	26	0.0	2.0	5	0	26	0.0	5.2	10	0	16	12.3	11.7	2	1	12	19.6	20.5	6	1	17	0.0	5.4
1	0	27	12.2	12.5	5	0	27	7.8	7.3	10	0	17	6.0	6.4	2	1	13	15.5	15.2	6	1	18	9.2	10.0
1	0	28	11.9	11.2	6	0	0	54.6	52.8	10	0	18	0.0	2.7	2	1	14	16.9	16.9	6	1	19	20.3	23.5
1	0	29	0.0	1.6	6	0	1	23.0	22.1	10	0	19	12.2	11.5	2	1	15	10.8	10.3	6	1	20	8.4	8.8
1	0	30	10.2	9.4	6	0	2	13.8	13.6	10	0	20	6.0	3.6	2	1	16	35.8	35.5	6	1	21	11.5	12.6
2	0	0	9.4	9.3	6	0	3	3.0	2.6	10	0	21	0.0	7.1	2	1	17	32.1	30.4	6	1	22	0.0	1.1
2	0	1	3.5	3.4	6	0	4	0.0	2.2	11	0	1	15.8	16.2	2	1	18	12.5	11.5	6	1	23	0.0	2.5
2	0	2	46.7	48.8	6	0	5	36.9	36.8	11	0	2	0.0	6.4	2	1	19	0.0	2.7	6	1	24	13.5	14.9
2	0	3	103.1	116.9	6	0	6	41.8	40.3	11	0	3	10.0	10.1	2	1	20	0.0	4.7	6	1	25	11.7	11.0
2	0	4	86.5	85.6	6	0	7	12.3	13.1	11	0	4	0.0	2.7	2	1	21	0.0	3.2	6	1	26	0.0	1.1
2	0	5	16.0	17.1	6	0	8	12.6	12.9	11	0	5	23.5	24.2	2	1	22	23.4	26.9	6	1	27	6.9	7.4
2	0	6	17.9	17.5	6	0	9	5.6	5.3	11	0	6	12.2	12.5	2	1	23	17.7	21.4	7	1	0	0.0	2.7
2	0	7	18.4	17.9	6	0	10	17.8	16.0	11	0	7	0.0	2.5	2	1	24	0.0	1.2	7	1	2	35.7	34.3
2	0	8	6.9	6.5	6	0	11	26.9	26.6	11	0	8	9.8	9.2	2	1	25	0.0	2.8	7	1	3	0.0	2.2
2	0	9	48.5	46.5	6	0	12	13.4	11.7	11	0	9	18.3	19.1	2	1	26	0.0	1.1	7	1	4	34.1	31.7
2	0	10	50.8	47.6	6	0	13	33.0	30.5	11	0	10	0.0	1.8	2	1	27	0.0	3.4	7	1	5	23.0	21.4
2	0	11	26.3	27.6	6	0	14	0.0	0.6	11	0	11	15.5	16.0	2	1	28	12.0	11.9	7	1	6	0.0	0.7
2	0	12	20.3	19.2	6	0	15	5.7	7.5	11	0	12	14.2	14.4	2	1	29	7.4	8.0	7	1	7	20.8	20.8
2	0	13	8.6	8.4	6	0	16	17.4	19.8	11	0	13	0.0	3.1	3	1	1	50.2	51.6	7	1	8	23.2	22.1
2	0	14	26.5	25.7	6	0	17	13.0	15.1	11	0	14	9.2	8.2	3	1	2	0.0	1.7	7	1	9	0.0	2.9
2	0	15	0.0	3.4	6	0	18	11.7	13.2	11	0	15	15.0	12.4	3	1	3	8.1	9.1	7	1	10	21.6	20.1
2	0	16	11.5	11.3	6	0	19	23.9	26.1	11	0	16	5.5	5.3	3	1	4	13.5	14.0	7	1	11	29.4	27.5
2	0	17	30.7	28.7	6	0	20	0.0	5.6	11	0	17	0.0	1.8	3	1	5	25.1	27.5	7	1	12	0.0	0.4
2	0	18	11.3	11.0	6	0	21	0.0	4.1	11	0	18	10.7	10.2	3	1	6	27.9	31.5	7	1	13	32.2	29.3
2	0	19	0.0	0.4	6	0	22	12.3	12.5	11	0	19	6.0	2.1	3	1	7	35.1	39.2	7	1	14	0.0	4.2
2	0	20	22.8	26.3	6	0	23	0.0	6.8	12	0	0	0.0	0.3	3	1	8	9.0	5.7	7	1	15	0.0	4.6
2	0	21	19.0	21.5	6	0	24	18.9	16.7	12	0	1	0.0	4.6	3	1	9	7.0	7.2	7	1	16	0.0	5.5
2	0	22	0.0	3.6	6	0	25	14.2	10.3	12	0	2	12.8	11.4	3	1	10	9.2	12.4	7	1	17	21.5	18.3
2	0	23	16.3	16.3	6	0	26	0.0	0.1	12	0	3	14.7	15.3	3	1	11	0.0	3.5	7	1	18	0.0	1.4
2	0	24	0.0	0.4	6	0	27	0.0	0.1	12	0	4	0.0	4.2	3	1	12	67.6	70.9	7	1	19	13.8	14.9
2	0	25	0.0	2.6	7	0	1	0.0	2.4	12	0	5	10.0	10.3	3	1	13	15.8	15.5	7	1	20	6.4	6.7
2	0	26	15.7	16.2	7	0	2	35.7	34.7	12	0	6	0.0	2.3	3	1	14	0.0	0.1	7	1	21	12.2	12.6
2	0	27	16.1	15.7	7	0	3	13.4	12.9	12	0	7	0.0	4.1	3	1	15	0.0	1.3	7	1	22	0.0	6.1
2	0	28	0.0	3.3	7	0	4	0.0	2.3	12	0	8	13.0	11.9	3	1	16	0.0	2.9	7	1	23	0.0	2.4
2	0	29	0.0	0.7	7	0	5	0.0	3.5	12	0	9	6.2	6.3	3	1	17	10.2	10.3	7	1	24	0.0	3.1
2	0	30	0.0	5.9	7	0	6	17.0	17.1	12	0	10	5.4	6.3	3	1	18	44.5	41.1	7	1	25	0.0	0.3
3	0	0	103.8	101.6	7	0	7	10.6	10.0	12	0	11	10.7	9.8	3	1	19	0.0	1.9	8	1	0	12.9	12.0
3	0	2	26.0	26.1	7	0	8	45.0	44.6	12	0	12	0.0	4.9	3	1	20	5.7	8.9	8	1	1	22.5	20.4
3	0	3	27.8	27.6	7	0	9	29.9	28.4	12	0	13	13.9	12.8	3	1	21	0.0	1.8	8	1	2	0.0	4.4
3	0	4	15.4	15.9	7	0	10	10.5	10.2	12	0	14	9.9	8.4	3	1	22	10.8	13.5	8	1	3	29.8	27.7
3	0	5	36.1	35.0	7	0	11	9.7	9.3	12	0	15	0.0	4.2	3	1	23	0.0	5.3	8	1	4	8.2	7.4
3	0	6	41.6	46.9	7	0	12	15.2	14.8	12	0	16	13.5	11.7	3	1	24	11.0	11.8	8	1	5	0.0	4.3
3	0	7	90.6	89.1	7	0	13	16.0	14.8	12	0	17	0.0	4.4	3	1	25	5.9	6.4	8	1	6	12.7	11.7
3	0	8	7.0	6.2	7	0	14	20.0	21.8	13	0	0	0.0	5.1	3	1	26	11.0	11.3	8	1	7	28.7	26.7
3	0	9	42.2	40.3	7	0	15	24.1	28.0	13	0	2	20.1	19.5	3	1	27	0.0	4.9	8	1	8	14.5	13.9
3	0	10	6.4	7.0	7	0	16	6.5	6.9	13	0	3	0.0	3.1	3	1	28	12.4	12.4	8	1	9	6.4	6.4
3	0	11	0.0	4.5	7	0	17	10.1	11.5	13	0	4	13.9	13.2	3	1	29	0.0	3.4	8	1	10	15.2	13.5
3	0	12	34.2	33.3	7	0	18	0.0	4.4	13	0	5	0.0	0.5	4	1	0	18.4	17.2	8	1	11	27.4	24.8
3	0	13	37.1	35.9	7	0	19	17.5	11.5	13	0	6	6.4	5.9	4	1	1	43.9	42.3	8	1	12	0.0	5.2
3	0	14	9.4	9.2	7	0	20	0.0	2.2	13	0	7	8.5	8.7	4	1	2	48.1	46.4	8	1	13	18.2	16.1
3	0	15	23.0	21.3	7	0	21	17.7	18.3	13	0	8	17.7	17.4	4	1	3	71.1	70.2	8	1	14	13.6	11.0
3	0	16	7.4	6.8	7	0	22	0.0	4.0	13	0	9	6.0	5.5	4	1	4	47.0	46.2	8	1	15	9.8	9.1
3	0	17	10.8	9.8	7	0	23	9.2	8.1	13	0	10	0.0	2.1	4	1	5	33.3	32.4	8	1	16	14.3	15.2
3	0	18	16.8	15.2	7	0	24	0.0	3.5	13	0	11	0.0	2.6	4	1	6	7.3	6.6	8	1	17	25.8	27.9
3	0	19	4.0	2.0	7	0	25	5.1	4.8	13	0	12	7.6	7.1	4	1	7	36.7	34.8	8	1	18	0.0	4.5
3	0	20	7.7	8.6	8	0	0	181.0	20.4	13	0	13	6.6	6.4	4	1	8	15.9	15.0	8	1	19	0.0	5.7
3	0	21	0.0	2.5	8	0	1	0.0	2.1	14	0	0	4.3	4.2	4	1	9	36.5	37.8	8	1	20	4.9	5.1
3	0	22	0.0	4.8	8	0	2	46.8	41.9	14	0	1	0.0	3.7	4	1	10	15.3	15.2	8	1	21	10.2	10.2
3	0	23	0.0	6.9	8	0	3	33.8	32.5	14	0	2	12.2	11.5	4	1	11	17.7	17.9	8	1	22	10.7	10.2
3	0	24	7.7	7.5	8	0	4	34.3	31.0	14	0	3	0.0	1.9	4	1	12	0.0	1.8	8	1	23	17.8	17.9
3	0	25	17.4	18.0	8	0	5	0.0	1.8	14	0	4	9.1	9.0	4	1	13	11.5	10.4	8	1	24	6.1	6.0
3	0	26	0.0	5.3	8	0	6	19.6	17.6	14	0	5	5.0	5.2	4	1	14	10.9	11.2	8	1	25	0.0	2.3
3	0	27	6.7	6.5	8	0	7	10.2	9.5	14	0	6	0.0	1.8	4	1	15	11.0	10.9	9	1	1	31.9	28.4
3	0	28	0.0	1.9	8	0	8	27.4	25.1	14	0	7	10.8	9.3	4	1	16	9.9	8.9	9	1	2	14.3	13.0
3	0	29	0.0	4.2	8	0	9	13.2	11.9	0	1	1	0.0	51.3	4	1	17	0.0	1.5	9	1	3	8.9	8.1
4	0	0	9.4	10.7	8	0	10	0.0	5.5	0	1	3	43.8	44.4	4	1	18	13.6	13.1	9	1	4	27.6	25.7
4	0	1	63.7	60.9	8	0	11	0.0	1.9	0	1	5	101.0	99.2	4	1	19	11.0	9.7	9	1	5	15.3	13.5
4	0	2	0.0	2.2	8	0	12	11.7	13.1	0	1	7	34.1	31.0	4	1	20	22.0	19.8	9	1	6	13.2	12.0
4	0	3	33.2	31.9	8	0	13	10.2	12.1	0	1	9	19.3	17.2	4	1	21	7.7	6.8	9	1	7	36.8	32.5
4	0	4	32.5	31.4	8	0	14	0.0	0.4	0	1	11	58.3	56.0	4	1	22	11.9	14.0	9	1	8	0.0	4.2
4	0	5	29.8	29.0	8	0	15	0.0	2.5	0	1	13	58.3	55.8	4	1	23	7.6	7.8	9	1	9	11.4	12.9
4	0	6	4.7	5.7	8	0	16	13.7	12.3	0	1	15	10.7	10.0	4	1	24	6.5	7.1	9	1	10	21.2	19.2
4	0	7	32.6	31.2	8	0	17	0.0	2.3	0	1	17	18.3	17.4	4	1	25	12.1	11.7	9	1	11	0.0	1.7
4	0	8	36.1	37.5	8	0	18	8.0	7.9	0	1	19	53.6	48.9	4	1	26	11.2	11.3	9	1	12	13.1	11.6
4	0	9	0.0	0.5	8	0	19	5.2	6.5	0	1	21	16.5	19.1	4	1	27	14.7	13.8	9	1	13	22.7	18.7
4	0	10	35.4	32.3	8	0	20	12.0	11.3	0	1	23	0.0	4.4	4	1	28	0.0	5.8	9	1	14	0.0	4.0
4	0	11	13.7	14.1	8	0	21	3.8	6.6	0	1	25	22.5	25.3	5	1	1	16.7	15.1	9	1	15	0.0	4.5
4	0	12	0.0	1.2	8	0	22	16.4	15.1	0	1	27	0.0	8.3	5	1	2	27.9	26.5	9	1	16	0.0	4.1
4	0	13	0.0	0.9	8	0	23	0.0	3.5	0	1	29	0.0	3.5	5	1	3	24.7	24.6	9	1	17	0.0	4.7
4	0	14	47.8	44.4	8	0	24	0.0	0.5	1	1	1	25.3	28.8	5	1	4	18.9	19.9	9	1	18	0.0	4.7

Table 3. Continued.

h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$
9	1	19	0.0	0.3	10	1	18	7.2	7.5	12	1	0	25.7	27.7	13	1	7	13.1	13.7	2	7	0	0.0	0.4
9	1	20	0.0	2.4	10	1	19	3.9	4.3	12	1	1	0.0	1.4	13	1	8	4.2	4.1	4	2	0	6.8	7.8
9	1	21	0.0	2.3	10	1	20	23.3	21.4	12	1	2	0.0	4.9	13	1	9	6.7	6.0	4	3	0	9.8	10.2
9	1	22	4.7	5.0	10	1	21	6.8	6.3	12	1	3	16.5	18.5	13	1	10	0.0	2.6	4	4	0	4.1	4.8
9	1	23	0.0	6.2	11	1	1	20.5	16.5	12	1	4	0.0	0.6	13	1	11	15.1	14.2	4	5	0	6.4	6.1
10	1	0	17.5	16.0	11	1	2	0.0	1.9	12	1	5	0.0	4.1	13	1	12	9.3	8.5	4	6	0	0.0	3.1
10	1	1	0.0	4.5	11	1	3	0.0	0.8	12	1	6	19.3	19.3	13	1	13	13.4	12.6	4	7	0	0.0	3.3
10	1	2	11.1	10.3	11	1	4	16.4	16.8	12	1	7	0.0	0.1	14	1	0	15.9	15.5	6	2	0	44.1	42.7
10	1	3	9.2	19.0	11	1	5	14.9	15.2	12	1	8	0.0	1.2	14	1	1	5.5	6.6	6	3	0	46.8	44.2
10	1	4	24.3	20.4	11	1	6	0.0	1.9	12	1	9	10.4	11.0	14	1	2	9.7	9.3	6	4	0	32.0	28.5
10	1	5	0.0	3.4	11	1	7	9.0	9.9	12	1	10	8.9	8.7	14	1	3	9.9	9.6	6	5	0	29.8	27.8
10	1	6	11.6	10.5	11	1	8	13.0	13.0	12	1	11	6.8	7.5	14	1	4	8.9	8.3	6	6	0	16.7	17.2
10	1	7	0.0	1.5	11	1	9	0.0	4.1	12	1	12	0.0	3.7	14	1	5	0.0	2.9	8	2	0	0.0	17.7
10	1	8	11.6	10.4	11	1	10	21.9	21.5	12	1	13	0.0	0.7	14	1	6	0.0	11.9	8	3	0	10.8	9.5
10	1	9	12.3	10.5	11	1	11	6.9	7.4	12	1	14	0.0	2.6	14	1	7	4.8	5.1	8	4	0	14.7	12.3
10	1	10	15.7	17.1	11	1	12	0.0	3.1	12	1	15	0.0	0.3	0	2	0	132.8	166.2	8	5	0	6.5	6.5
10	1	11	0.0	0.2	11	1	13	0.0	1.8	12	1	16	9.7	9.0	0	4	0	73.4	78.6	8	6	0	6.0	7.0
10	1	12	0.0	0.7	11	1	14	16.3	15.8	13	1	1	0.0	3.5	0	6	0	36.2	42.5	10	2	0	9.6	8.0
10	1	13	0.0	2.7	11	1	15	7.1	6.3	13	1	2	0.0	1.3	2	2	0	8.1	7.1	10	3	0	11.8	13.0
10	1	14	23.6	24.3	11	1	16	14.6	13.9	13	1	3	0.0	1.6	2	3	0	3.5	4.1	10	4	0	5.6	5.7
10	1	15	0.0	1.0	11	1	17	0.0	0.9	13	1	4	0.0	2.1	2	4	0	0.0	3.4	10	5	0	8.0	8.8
10	1	16	9.8	9.5	11	1	18	6.9	6.6	13	1	5	10.3	10.5	2	5	0	0.0	1.8	12	2	0	0.0	0.1
10	1	17	0.0	0.7	11	1	19	0.0	3.7	13	1	6	6.7	6.2	2	6	0	0.0	2.1	12	3	0	22.3	22.4
																				12	4	0	0.0	0.1

The y parameters for the chromium positions deviated from 0.25 by less than two times the standard deviations calculated, while the deviations for the carbon atoms were somewhat larger. However, the deviations from *Pnma* symmetry observed can hardly be regarded as significant. Accordingly, it is concluded that the Cr_3C_2 structure has the symmetry of space group *Pnma*.

Table 4. Interatomic distances (Å units) and their standard deviations in Cr_3C_2. Distances shorter than 3.4 Å are listed.

	Dist.	S.d.		Dist.	S.d.
Cr1 — 2 C2	2.040	0.005	C1 — 2 Cr2	2.020	0.005
— C2	2.260	0.007	— 2 Cr2	2.111	0.005
— C1	2.290	0.007	— 2 Cr3	2.125	0.005
— 2 Cr3	2.582	0.001	— Cr1	2.290	0.007
— C1	2.618	0.007	— Cr1	2.618	0.007
— 2 Cr2	2.640	0.001	— 2 C1	2.829	0.000
— 2 Cr1	2.669	0.002	— 2 C1	2.944	0.005
— 2 Cr2	2.689	0.001	— 2 C2	2.978	0.009
— Cr3	2.735	0.001	— C2	3.005	0.010
— 2 Cr1	2.829	0.000	— 2 C2	3.289	0.009
Cr2 — 2 C1	2.020	0.005	C2 — 2 Cr3	2.031	0.005
— C2	2.087	0.007	— 2 Cr1	2.040	0.005
— 2 C1	2.111	0.005	— Cr3	2.069	0.007
— Cr3	2.500	0.001	— Cr2	2.087	0.007
— Cr3	2.570	0.001	— Cr1	2.260	0.007
— 2 Cr1	2.640	0.001	— 2 C2	2.829	0.000
— 2 Cr1	2.689	0.001	— 2 C1	2.978	0.009
— 2 Cr2	2.819	0.000	— C1	3.005	0.010
— 2 Cr2	2.829	0.000	— 2 C2	3.199	0.013
			— 2 C1	3.289	0.009
Cr3 — 2 C2	2.031	0.005	— 2 C2	3.378	0.013
— C2	2.069	0.007			
— 2 C1	2.125	0.005			
— Cr2	2.500	0.001			
— 2 Cr3	2.565	0.002			
— Cr2	2.570	0.001			
— 2 Cr1	2.582	0.001			
— Cr1	2.735	0.001			
— 2 Cr3	2.829	0.000			

The final structure data obtained from the intensity material measured by the scintillation counter technique are presented in Table 2. The corresponding list of calculated and observed (absorption- and extinction-corrected) structure factors is given in Table 3. Interatomic distances with their standard deviations are given in Table 4.

A comparison of the structure data obtained by the photographic method with those obtained with the counter method shows an excellent agreement between the positional parameters, while the agreement between the temperature factors is less satisfactory. This discrepancy may at least partly be due to the remaining extinction errors in the photographic intensity material. There is also the possibility of a systematic error in the visual intensity estimation. The white radiation streaks on Weissenberg films taken with molybdenum radiation are rather strong, and this might cause the estimation of the strong low-angle reflexions to be too low in comparison with the weaker high-angle intensities.

It is interesting to compare the values in Table 2 with the chromium parameters obtained by H and W and the carbon parameters reported by Meinhardt and Krisement. The chromium parameters according to H and W are as follows: for Cr1 $x=0.031$, $z=0.406$; for Cr2 $x=0.175$, $z=0.770$ and for Cr3 $x=0.850$, $z=0.930$. Meinhardt and Krisement gave the following carbon parameters: for C1 $x=0.092$, $z=0.204$ and for C2 $x=0.228$, $z=0.952$. Considering the differences in the experimental methods used, the agreement between the older values and those obtained in the present study is quite good.

DESCRIPTION AND DISCUSSION OF THE Cr_3C_2 STRUCTURE

A projection of the Cr_3C_2 structure on (010) is shown in Fig. 1.

The nearest neighbours to each of the two types of carbon atom are six chromium atoms situated at the corners of triangular prisms. The average of

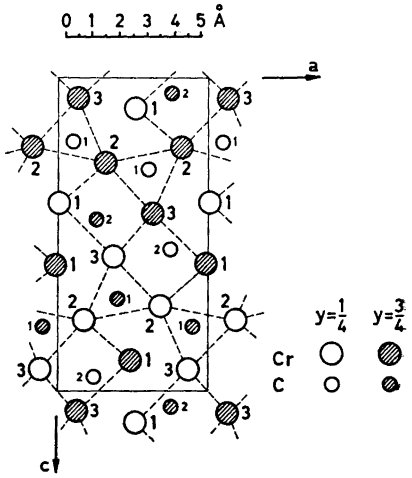

Fig. 1. The structure of Cr_3C_2 projected on (010). The triangular Cr_6C prisms are indicated by broken lines.

the six C1—Cr distances is 2.09 Å, and the corresponding value for the C2—Cr distances is 2.05 Å. In addition to the six nearest chromium atoms, the carbon atoms have further chromium neighbours situated outside the foursided faces of the prisms. C2 has one chromium neighbour at 2.26 Å and C1 has two chromium neighbours at 2.29 Å and 2.62 Å, respectively.

The triangular prismatic coordination of six metal atoms about a central nonmetal atom, with 0—3 additional metal atoms situated outside the quadrilateral faces of the prism, is very common with metal-rich compounds containing transition metals and elements with unfilled *p* levels. Numerous examples are found among the transition metal borides, carbides, silicides, germanides, phosphides, arsenides, sulfides, and selenides. The augmented triangular prismatic coordination, in particular the nine-coordination, has been the subject of thorough geometric analyses.[5,10] If the structures are regarded as closely packed arrays of rigid, spherical atoms, it is possible to predict the interatomic distances with a fair degree of accuracy, using the Goldschmidt radii for 12-coordination for the metal atoms and the tetrahedral covalent radii for the nonmetal atoms. Following this approach, Lundström [7] observed in his comparison of the Hf_3P_2 and Cr_3C_2 structures that the size-factor effect might explain, why the distances from the central carbon atoms to the chromium atoms outside the prisms are very much larger than the C—Cr distances within the prisms, while in Hf_3P_2 the differences between the various Hf—P distances are rather small.

The structural relationships between the transition metal borides, carbides, *etc.*, as mentioned above, are very close for compounds containing less than about 40 at.% nonmetal. As the nonmetal content increases beyond 40 at.%, structural differences gradually become more pronounced. In particular, there is a strong tendency towards the formation of nonmetal-nonmetal bonds in the borides, silicides, and germanides, while nonmetal-nonmetal bonding occurs only at very high nonmetal contents in phosphides, arsenides, sulfides, and selenides. In transition metal carbides containing 50 at.% carbon or less, the C—C distances invariably exceed the C—C single-bond distance by more than 1 Å. As regards the tendency towards nonmetal-nonmetal bonding, the carbides are thus much more closely related to the phosphides than to the silicides or borides. For Cr_3C_2, the structural similarities to Hf_3P_2 have already been mentioned. In contrast, V_3B_2, Nb_3B_2, Ta_3B_2, Zr_3Si_2, and Hf_3Si_2, which are all isostructural,[6] contain pairs of boron or silicon atoms at bonding distances. As further examples of the structural similarities between carbides and phosphides the isostructural compounds WC and MoP, or the isostructural γ'-MoC, TiP, β-ZrP, and HfP may be mentioned.

Considering the limited crystal-chemical information available at the time of the first studies of the Cr_3C_2 structure, it is certainly not surprising that H and W assumed a close structural resemblance between Cr_3C_2 and FeB. Later, when the knowledge of the crystal chemistry of compounds between transition metals and *p* elements became more extensive, the original, incorrect Cr_3C_2 structure eventually appeared as an anomaly. With the final revision of the Cr_3C_2 structure, the crystal chemistry of the transition metal carbides forms a much more consistent pattern.

Acknowledgements. The authors wish to thank Professor G. Hägg for his kind interest and Dr. T. Lundström for valuable suggestions. The work has been supported by the *Swedish Natural Science Research Council.*

REFERENCES

1. Westgren, A. and Phragmén, G. *Kgl. Svenska Vetenskapsakad. Handl.* III, **8** (1926) No. 5.
2. Hellbom, K. and Westgren, A. *Svensk Kem. Tidskr.* **45** (1933) 141.
3. Bjurström, T. *Arkiv Kemi, Mineral., Geol.* **A 11** (1933) No. 5.
4. Meinhardt, D. and Krisement, O. *Z. Naturforsch.* **15a** (1960) 880.
5. Rundqvist, S. *Arkiv Kemi* **20** (1962) 67.
6. Aronsson, B., Lundström, T. and Rundqvist, S. *Borides, Silicides and Phosphides*, Methuen, London 1965.
7. Lundström, T. *Acta Chem. Scand.* **22** (1968) 2191.
8. *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham 1962, Vol. III.
9. Zachariasen, W. H. *Acta Cryst.* **18** (1963) 1139.
10. Aronsson, B. and Rundqvist, S. *Acta Cryst.* **15** (1962) 878.

Received September 11, 1968.