

X-RAY EXAMINATIONS OF CHROME ORES: (I) LATTICE DIMENSIONS; (II) THEORETICAL DENSITIES

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(I) LATTICE DIMENSIONS

As a part of an investigation of certain properties of chrome ores, the lattice dimensions of five chromites from various localities ranging in composition from 33% to 53% Cr_2O_3 were determined.

The diffraction patterns were obtained using a multiple unit apparatus, made by the General Electric Company. The radiations employed were $K\alpha$ doublet of molybdenum of the wave length 0.712 Å.U. The spacings were standardized with sodium chloride.

The length of the edge of the unit cube a_0 for the five ores, given in the table II is calculated from the two following equations of x-ray spectroscopy^{1,2}

$$\frac{d}{n} = \frac{\lambda}{2 \sin \theta} \quad (1)$$

$$a_0 = \frac{d_{hkl}}{n} \sqrt{(h^2 + k^2 + l^2)n^2} \quad (2)$$

d/n , the spacing measurements of the diffraction lines, recorded in the third column of the table II are for the chrome ore A. In the fourth column are given the estimated relative intensities for the same ore, assigning the brightest line a value of ten.

In the cubic system the ratios of $\sin^2 \theta$, (the latter being computed from the equation I) should give values which are integers and usually small. These values given in column five for A alone, diverge within the limits of the experimental error from the corresponding whole numbers given in the second column of the table II. The whole numbers represent the sum of $(h^2 + k^2 + l^2)n^2$ and aid in assigning the indices of the planes producing the diffraction pattern.

The ores examined were:

- A. Rhodesian African lump chrome ore
- B. Transvaal African lump chrome ore
- C. Grecian lump chrome ore
- D. Cuban lump chrome ore
- E. A high grade chrome ore, locality not known.

The ores for which no analyses were supplied were analyzed. In the case of the ores for which only partial (factory) analyses were available, the undetermined constituents were estimated in order to note roughly any obvious relationship existing between the lattice dimension and the chemical composition. The estimates were based upon the analyses of the typical ores found in the localities whence the ores were obtained. Publications on the mineral resources of U.S.³ and the records of the Geological Surveys were consulted in this connection. Two of the typical analyses of the Rhodesian and Grecian ores given by McDowell⁴ are:

	Rhodesian	Grecian
Cr ₂ O ₃	48.4	39.5
FeO	14.4	15.8
Al ₂ O ₃	12.1	26.2
MgO	14.2	15.8
SiO ₂	5.9	3.0
CaO	—	—

The estimates of the undetermined oxides of the Rhodesian (A) and Grecian (D) ores were partly based upon these. For Transvaal ore the estimates were based upon Wagner's⁵ work. Parantheses are placed around the figures which are estimated. The analyses of the ores are given in the table I.

TABLE I
ANALYSES OF THE CHROME ORES

	A Rhodesian	B Transvaal	C Cuban	D Grecian	E	Hungarian (Todoky ¹⁰)
Cr ₂ O ₃	47.14	42.68	33.83	37.74	53.08	54.22
SiO ₂	7.75	3.34	3.11	6.09	5.11	6.16
FeO	(15.00)	(27.00)	13.07	(15.00)	14.00	25.94
CaO			Trace		2.59	
MgO	(15.00)	(10.00)	17.61	(15.00)	8.95	9.77
Al ₂ O ₃	(13.00)	(15.00)	31.11	(26.00)	16.11	2.29
Loss on Ignition			1.12			
MnO						0.94
TiO ₂						0.68
H ₂ O						0.09
Total	97.89	98.02	99.85	99.83	99.84	100.09

The results seem to indicate that the values of a_0 for the different ores are inversely proportional to the Al_2O_3 content; or the higher the amount of aluminates present in the isomorphous mixture of spinels, the lower is the length of the edge of the unit cube (See Fig. 1).

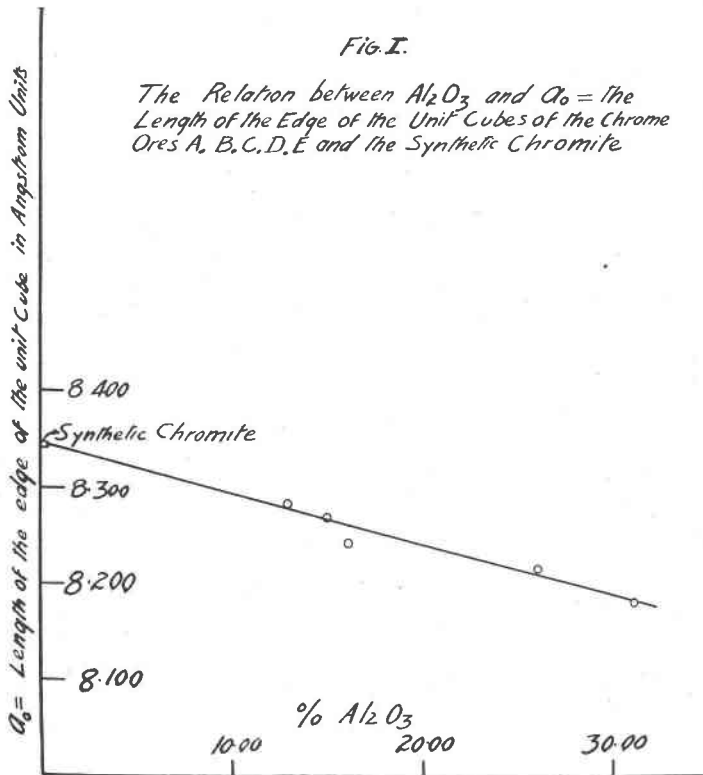


FIG. 1

Tests on synthetic spinels⁶ had shown that the structures of the chromites of Zn, Mg, Fe and Mn are generally intermediate between the structures of their ferrites and their aluminates. The lattice dimensions of the aluminates ranged from 8.062 to 8.271 Å.U.; those of the chromites varied from 8.296 to 8.436, the ferrites had the values between the limits of 8.423 to 8.457. Therefore, when either Al_2O_3 or Fe_2O_3 replaces Cr_2O_3 from the chromite molecule the value of a_0 should be lowered or raised in proportion to the replacement, in accordance with the additive law of Vegard.⁷

TABLE II
POWDER DIFFRACTION DATA FROM CHROME ORES

Indices	$(h^2+k^2+l^2)/n^2$	d/n	Estimated Intensity	Ratios of $\sin^2 \theta$	a_0 Chrome Ore A	a_0 Chrome Ore B	a_0 Chrome Ore C	a_0 Chrome Ore D	a_0 Chrome Ore E
111 (1)	3	4.80	5	2.98	8.31	8.29	8.19	8.23	8.24
110 (2)	8	2.93	6	79.90	8.28	8.28	8.17	8.23	8.25
113 (1)	11	2.499	10	11.00	8.29	8.26	8.19	8.21	8.23
111 (2)	12	2.390	v.f.	12.03	8.28	8.28	v.f.	v.f.	8.24
100 (4)	16	2.070	7	15.99	8.28	8.27	8.16	8.20	8.24
112 (2)	24	1.690	4	24.00	8.28	8.26	8.18	8.20	8.23
111 (3)	27	1.592	9	27.05	8.28	8.26	8.18	8.22	8.23
115 (1)									
110 (4)	32	1.461	9	32.14	8.27	8.27	8.18	8.22	8.26
135 (1)	35	1.398	v.f.	35.00	8.28	8.26	8.17	8.22	8.24
130 (2)	40	1.310	2	39.95	8.29	8.26	8.18	8.23	8.24
335 (1)	43	1.261	5	43.11	8.27	8.27	8.19	8.22	8.25
111 (4)	48	1.196	3	47.95	8.29	8.26	8.18	8.21	8.24
155 (1)	51	1.158	2	51.01	8.27	8.27	8.19	8.21	8.25
117 (1)									
123 (2)	56	1.107	3	55.90	8.29	8.26	8.16	8.23	8.24
355 (1)	59	1.079	6	58.91	8.28	8.27	8.18	8.22	8.23
137 (1)									
100 (8)	64	1.035	3	64.00	8.28	8.26	8.17	8.22	8.24
110 (6)	72	0.975	2	72.15	8.28	8.26	8.17	8.22	8.24
114 (2)									
111 (5)	75	0.956	4	75.01	8.28	8.26	8.17	8.20	8.24
157 (1)									
120 (4)	80	0.927	3	79.80	8.29	8.27	8.19	8.22	8.23
139 (1)	91	0.869	3	90.82	8.29	8.28	8.19	8.21	8.24
112 (4)	96	0.846	6	95.89	8.29	8.27	8.17	8.22	8.24
134 (2)	104	0.811	1	104.30	8.27	8.25	8.19	8.22	8.24
150 (2)									
159 (1)	107	0.801	4	106.89	8.28	8.27	8.17	8.21	8.24
377 (1)									
					8.283± 0.001	8.267± 0.001	8.179± 0.002	8.216± 0.001	8.241± 0.001

TABLE III

Synthetic Chromite ⁶	Rhodesian A	Transvaal B	E	Grecian D	Cuban C	Ural ⁹	Hungarian ¹⁰
8.344± 0.003	8.283± 0.001	8.267± 0.001	8.241± 0.001	8.216± 0.001	8.179± 0.002	8.355± 0.004; 8.358± 0.004	8.05

In this investigation it appears that Cr_2O_3 is replaced by Al_2O_3 alone since the values of a_0 gradually decline from the synthetic FeCr_2O_4 , which contains no Al_2O_3 to the Cuban ore which contains 31% Al_2O_3 . This seems to be further substantiated by the fact that the 5 ores examined are nonmagnetic while all the known ferrites, except ZnFe_2O_4 , are ferromagnetic and zinc seldom occurs in chromite.^{8,12}

It may be inferred that iron which is generally analyzed as Fe_2O_3 is present in these ores wholly in ferrous form (ferrous chromite, FeC_2O_4 ; ferrous aluminate, FeAl_2O_4) and not as ferrite.

No characteristic diffraction lines were observed for the minerals of SiO_2 and CaO , although they are not minerals of the spinel series. Their presence in the isomorphous spinel molecule whether interstitial or substitutional does not seem to have any marked effect on the lattice constants.

The x -ray data obtained by other investigators on chrome ores are given in the table III, together with those obtained in this investigation. Todoky's value of 8.05 Å.U. appears to be low considering the fact that it is a high grade chrome ore as revealed by its analysis (see Table I)

The quality of the chrome ore, it is evident, can not be definitely ascertained by means of x -ray examination; however, it can be roughly surmised as to its Al_2O_3 content.

(II) THEORETICAL DENSITIES

An attempt was made to compute the theoretical densities of the ores by employing the well known relation:

$$\rho = \frac{nM}{a_0^3}$$

in which ρ = density

n = number of molecules per unit cell;
8 in the case of spinels

M = molecular weight of the substance

a_0 = length of the edge of the unit cube.

The above equality holds true in the case of a substance composed only of a single kind of crystal. The ore is regarded as such, consisting of an isomorphous mixture of spinels.

The small amount of the mineral impurities in the ore (possibly due to the improper separation of chromite from gangue), some of these being visible under the microscope, yet giving no evidence of their presence in the diffraction patterns, were regarded, in order to

simplify the "average molecular weight" (M) computations, as being present within the chromiferous spinelled in solid solution. The value for M was determined from the mineral analysis of the ore. The following rules were observed in calculating the latter.

1. All Cr_2O_3 or FeO was regarded as entering the chromite molecule.
2. SiO_2 was disposed of as magnesium olivine— $2\text{MgO} \cdot \text{SiO}_2$; serpentine— $2\text{H}_2\text{O} \cdot 3\text{MgO} \cdot 2\text{SiO}_2$; or as uvarovite— $3\text{CaO} \cdot \text{Cr}_2\text{O}_3 \cdot 3\text{SiO}_2$; microscopic study determining the choice.
3. The remaining oxides were distributed to form the other members of the spinel series— $\text{MgO} \cdot \text{Cr}_2\text{O}_3$, $\text{MgO} \cdot \text{Al}_2\text{O}_3$, $\text{FeO} \cdot \text{Al}_2\text{O}_3$. The excess of either acidic or basic oxides, which practically all chrome ore analyses indicate, were reported as such—periclase (MgO) and corundum (Al_2O_3).
4. Ignition loss reported in the Cuban ore, C, was regarded as CO_2 and was disposed of as magnesite, MgCO_3 .

Taking, as an illustration, chrome ore C, for which a complete analysis was available, the percentages of the various oxides were divided by their molecular weights, and these were later combined to form different minerals, as is illustrated below.

$$\text{Mols. of various oxides} = \frac{\text{Percentage}}{\text{Molecular Weight}}$$

	Cr_2O_3	FeO	SiO_2	MgO	Al_2O_3	CO_2 (Ignition loss)
	0.2225	0.1821	0.0513	0.4371	0.3045	0.0254
0.1821 $\text{FeO} \cdot \text{Cr}_2\text{O}_3$	0.1821	0.1821				
0.0513 $2\text{MgO} \cdot \text{SiO}_2$			0.0513	0.1026		
Magnesium olivine						
0.0404 $\text{MgO} \cdot \text{Cr}_2\text{O}_3$	0.0404			0.0404		
0.0254 MgCO_3				0.0254		0.0254
Magnesite						
0.2686 $\text{MgO} \cdot \text{Al}_2\text{O}_3$				0.2686	0.2686	
spinel						
0.0359 Al_2O_3					0.0359	
Corundum						
0.6037 Total						

0.6037 is the combined mols. of different minerals present in 100 gms. of the ore. Therefore, the average molecular weight of the ore is $100/0.6037 = 165.6 = M$, and the density

$$\rho = \frac{8 \times 165.6 \times 1.649 \times 10^{-24}}{(8.179 \times 10^{-8})^3} = 3.989.$$

The mineral analyses, theoretical densities, and the true specific gravities of the chrome ores and the per cent difference between the theoretical and the actual values are given in the Table III.

It should be noted that the combined mols. of different minerals in each ore were uniformly divided into 100, to obtain the average molecular weight of the ore, regardless of the fact that the analyses slightly deviated from this sum.

In the case of A, in order to form 0.0646 mols. of serpentine, the presence of which was confirmed by microscopic examination of the ore, 2.33% H₂O is necessary. This is not provided for in the analysis for A (Table) where only the three main unanalyzed constituents were estimated. However, when 2.33% H₂O is added to 97.89% already accounted for the sum approaches about 100%, which, as mentioned above, was used in the average molecular weight calculation.

The sum of analyzed and unanalyzed oxides totaled 98.02% in the case of B (See table I); the total number of mols. of different minerals was slightly smaller and the theoretical density and the "average molecular weight" were a little larger due to the fact that 100 was used as the basis instead of the actual value of 98.02%. In this particular case the deviation between the theoretical and the actual densities was found to be the maximum, 5.93%.

This method of computing the theoretical density of the ore by calculating an "average molecular weight" from the chemical composition should be applicable to all substances¹¹ forming continuous solid solutions and obeying the additive law of Vegard.

SUMMARY

Diffraction data by the "powder method" were obtained from 5 chrome ores found in various localities. The length of the edge of the unit cube ranged from 8.283 ± 0.001 to 8.179 ± 0.002 , varying inversely with the Al₂O₃ content of the ore.

A method which has been applied to alloys for computing the theoretical density has been extended for calculating the "average molecular weight" of the chrome ore; this method is generally applicable to substances, forming isomorphous mixtures and continuous substitutional solid solutions which obey the additive law of Vegard. The theoretical densities of the 5 ores obtained by this method had a maximum difference of 1.3% between the theoretical and the actual values in the case of ores with complete analyses

TABLE III
THE MINERAL ANALYSES, THEORETICAL DENSITIES, AND THE TRUE SPECIFIC GRAVITIES OF THE CHROME ORES

	A	B	C	D	E	Synthetic
	Rhodesian	Transvaal	Cuban	Grecian		Chromite
FeO · Cr ₂ O ₃ (Chromite)	0.2089	0.2808	0.1821	0.2090	0.1951	
MgO · Cr ₂ O ₃ (Magnochromite)	0.1012		0.0404	0.0391	0.1384	
MgO · Al ₂ O ₃ (Spinel)	0.0772	0.0515	0.2686	0.2421	0.0065	
2MgO · SiO ₂ (Magnesium olivine)		0.0554	0.0513	0.1010	.0386	
2H ₂ O · 3MgO · 2SiO ₂ (Serpentine)	0.0646					
3CaO · Cr ₂ O ₃ · 3SiO ₂ (Uvarovite)			0.0254		0.0154	
MgCO ₃ (Magnesite)		0.0857				
MgO (Periclase)	0.0500		0.0359	0.0133	0.1511	
Al ₂ O ₃ (Corundum)						
FeO · Al ₂ O ₃ (Hercynite)		0.0952				
Total No. of Mols. in 100 gms. of the ore	0.5019	0.5686	0.6037	0.6045	0.5451	
Average Molecular Weight	199.1	175.8	165.6	165.3	183.3	
Theoretical Density	4.619	4.145	3.989	3.934	4.245	5.085
True Specific Gravity D ²⁰ / ₂₀	4.421	3.913	3.980	3.888	4.191	4.998
Difference between theoretical and actual densities in per cent.	4.79%	5.93%	0.226%	1.18%	1.29%	1.74%

available, and a maximum difference of 5.93% where some of the undetermined constituents were estimated.

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