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X-ray Diffraction Data for Large Aromatic Molecules

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This paper presents new theoretical data for the intensity of X-rays diffracted from randomly orientated perfect aromatic molecules, such as are found in amorphous carbons. The data have been computed numerically on the EDSAC, using the Debye radial distribution function.

Introduction

Various workers, notably Warren (1941), Wilson (1949) and Brindley & Méring (1951), have given theoretical expressions for the line profiles of diffraction bands due to randomly orientated layer structures. Each of these writers approached the problem by calculating the interference function $I(\mathbf{s})$ as a function of the position vector $\mathbf{s}$ in reciprocal space, and then performing an integration over the surface of a sphere of radius s to account for the effect of the random orientation. Some approximation was always necessary in performing the spherical integration, and, though these approximations introduce little error in the case of large layers, their effects can be quite serious if the layers are very small, when the interference function has appreciable values throughout a large region of reciprocal space. In general, the interference function can be expressed as

$$I(\mathbf{s}) = (FF^*).\widehat{(GG^*)(HH^*)} ,$$

in which G is the transform of the lattice, H is the transform of the shape of the layer and F is the structure factor of the unit cell within the layer. In their algebraic calculations, the previous workers were obliged to take the factor (FF^*) outside the integral sign when performing the spherical integration, whereas the data now presented make the correct allowance for variations in F, G and H.

The calculations leading to the present data, while being less general than those of the previous workers, are exact in that the algebraical difficulties are completely overcome by the use of the Debye radial distribution formula

$$J(s) = \sum_r \frac{n(r)}{N} \frac{\sin 2\pi rs}{2\pi rs} ,$$

in which $J(s)$ is the intensity in atomic units scattered at any angle 2θ, where $s = 2 \sin \theta/\lambda$, $n(r)$ is the number of interatomic vectors of length r within the layer, irrespective of direction, and N is the total number of atoms in the layer.

The resulting curves are completely specific to the case of perfect two-dimensional molecules of the type shown in Fig. 1, which are of importance in any study of amorphous carbons. All the atoms are assigned equal weight, all the bonds are taken to be of equal length l, and all the inter-bond angles are 120°. The calculation then provides a table of values of $J(s)$ against s, without making any approximations and without the need to give separate consideration to each (hk) band.

Details of the calculation

The method consists essentially in choosing (in every case except one) four molecules of arbitrary shape but of a particular size range, constructing their Patterson functions, adding these together, dividing by the total number of atoms in the four molecules to normalize to a scale of scattering per atom, and inverting the result by the Debye formula.

The reason for the use of four molecules is to obtain a scattering curve which is characteristic of a particular size range but with the effects of particular shapes eliminated as far as possible. Fig. 2 shows an example of a curve calculated for a parallelogram-shaped molecule, which shows marked secondary diffraction ripples in the region of s just less than that at which the intensity begins to rise towards a peak. The presence of these ripples emphasizes the need to avoid special shapes. Effects such as this are minimized in the tabulated data.

Each class of molecules corresponding to a particular size range is described by a number, which is arbitrary except that it increases with increasing size of the molecules. Fig. 1 shows the molecules with odd class numbers used in some of the calculations, (similar molecules were used to obtain intermediate curves with even class numbers). The quantity L is a nominal layer diameter in Ångströms, being given by

$$L = 2{\cdot}5\sqrt{(\tfrac{1}{2}N)} = 1{\cdot}768\sqrt{N} ,$$

where L is the length of the edge of a 60° rhombus the edges of which are parallel to the two-dimensional hexagonal unit cell of side 2·5 Å and containing two

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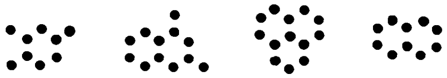
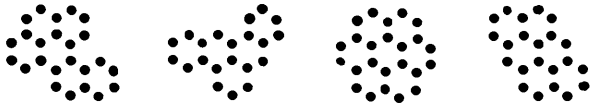
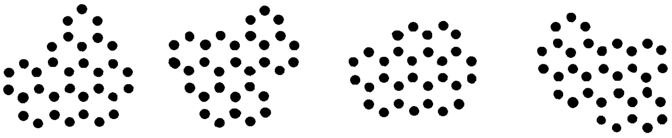
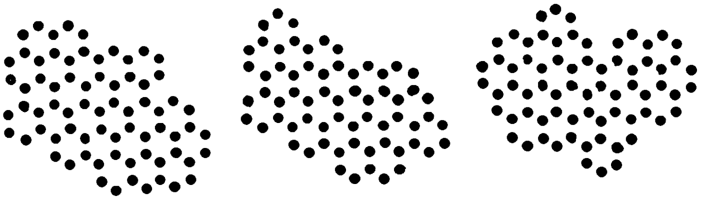
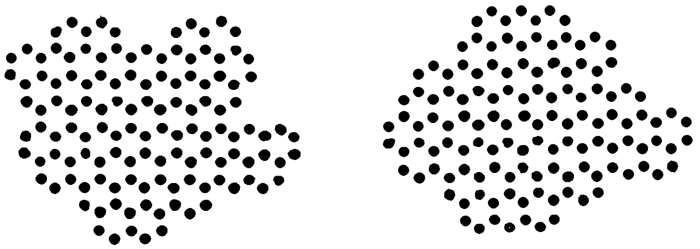
Class	L (Å)	Number of atoms	Molecular weight	Molecules used
1	5.8	11	132	
3	8.4	22	273	
5	10	32	387	
7	15	72	860	
9	20	128	1536	

Fig. 1. The molecules used in the calculations.

atoms per cell; the rhombus contains the same number of atoms as the molecules used in the calculation.

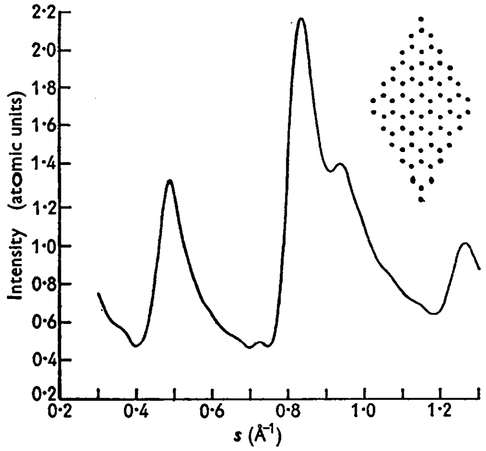


Fig. 2. Diffraction from a parallel-sided molecule.

This definition is clearly arbitrary, as the linear dimensions of a molecule are related to $\sqrt{N}$ in a manner depending on shape.

The Patterson functions were obtained by making two representations of each molecule on separate sheets of tracing paper, in one of which the atoms were represented by points, and in the other by rings. The two sheets were then superimposed so that one representation was displaced parallel to the other by each and every possible lattice displacement, the number of points with rings round them being counted and the total written through a small hole in the upper sheet for each displacement, thus generating the Patterson function on the lower sheet. The coefficients $n(r)$ were then obtained by collecting together the numbers of all the vectors distant r from the origin of the Patterson function, r being equal to $l\sqrt{(u^2-uv+v^2)}$, in which l is the bond length and u, v and w are hexagonal coordinates in the plane of Patterson space with the coefficient, w, of the third axis set equal to zero.

In the case of the curve for $L = 30$ Å, the spot counting method was abandoned. Instead, a graph of $n(r)/Nm$ versus r/L was drawn, using the spot-counts for $L = 15$, 17·5 and 20 Å (Fig. 3 and Table 1), from which the coefficients for the $L = 30$ Å curve were obtained, after allowing for the multiplicity factor by multiplying by m (Table 2).

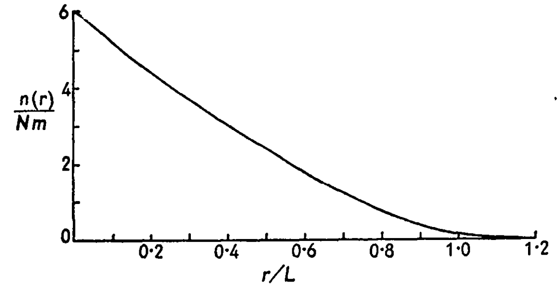


Fig. 3. Graph of the function $n(r)/Nm$ versus r/L.

Table 1. *Tabulation of* $n(r)/Nm$ *for* $0 \leq r/L \leq 1{\cdot}18$ *by increments of* 0·02

6·000	5·870	5·725	5·565	5·395
5·205	5·025	4·855	4·690	4·540
4·390	4·250	4·105	3·965	3·820
3·680	3·540	3·405	3·270	3·140
3·005	2·880	2·750	2·620	2·505
2·380	2·255	2·130	2·010	1·895
1·780	1·655	1·540	1·425	1·320
1·215	1·115	1·015	0·920	0·825
0·735	0·650	0·570	0·500	0·435
0·370	0·310	0·255	0·210	0·175
0·145	0·110	0·095	0·080	0·060
0·045	0·035	0·025	0·015	0·005

Table 2. *Tabulation of m*

Case	m	Conditions
1	$\frac{1}{6}$	At the origin, i.e. if $u = v = w = 0$
2	$\frac{1}{2}$	On a possible mirror line, i.e. either (*a*) if any *two* of u, v, w equal one another; or (*b*) if $(u+v+w) = 0$ with any *one* of u, v, or w equal to zero
3	2	If $(u+v+w)$ is divisible by 3
4	1	Otherwise, or if cases 2 and 3 arise together

The quantity r/L was calculated, using a bond length of 1·4174 Å or kX. (the units being the same as those of the X-ray wavelength), and in using the data for $n(r)/Nm$, r had to be taken as $1{\cdot}4174\sqrt{(u^2-uv+v^2)}$ and L as $2{\cdot}5\sqrt{(\frac{1}{2}N)}$, even if a bond length other than 1·4174 Å had been used in the remainder of the calculation, otherwise incorrectly normalized figures would have resulted.

The numerical and graphical data

The results of these calculations are shown graphically in Fig. 4, together with one comparison with a curve obtained by the method of Warren (1941). Evidently Warren's method over-emphasizes the peaks at the expense of the fringes on the low-angle side of each peak. Wilson (1949) and Brindley & Méring (1951) both reported that the Warren function for a single peak was too high; the present work confirms this and also indicates that the 'tails' of the Warren function are too low. Closer investigation indicates, however, that the differences near $s = 0{\cdot}35$ and $0{\cdot}70$ Å^{-1} are due to a spreading of intensity from the peaks at

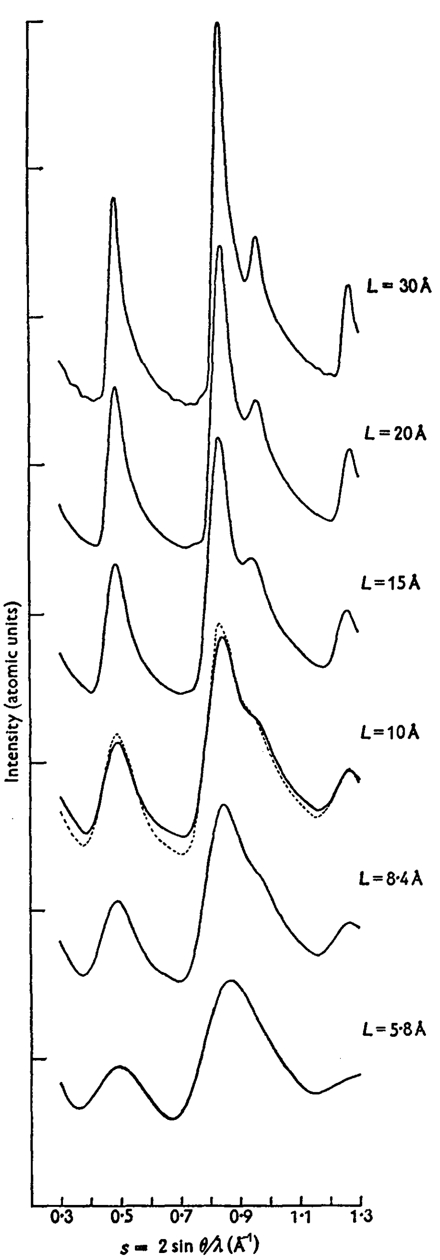


Fig. 4. The calculated intensities, together with a comparison between the curve for $L = 10$ Å and a curve calculated by the method of Warren (1941) (broken line) for a similar layer size.

$s = 0·49$ and 0·83 Å^{-1} respectively, and really represent diffuse secondary diffraction ripples, which are better accounted for by the present method of calculation.

Values of $J(s)$ are also given in tabular form in Table 3; the data being given for $0·01 \leq s \leq 1·50$ Å^{-1} by intervals of 0·01 Å^{-1}, from column to column, and of 0·10 Å^{-1} from row to row. The results of similar calculations for molecules of even class numbers are given by Diamond (1956).

In addition to the calculations described above for perfectly regular molecules, two calculations have been performed on slightly irregular molecules in order to estimate the importance of the variations in bond length which occur in such small layers (for details see Diamond (1956)). To this end, inter-atomic vector lengths derived from the experimental data for pyrene and for coronene given by Robertson & White (1945, 1947), and Robertson (1951) were used in the Debye formula, and the results were compared with those

Table 3. *Tabulation of* $J(s)$ *for* $0·01 \leq s \leq 1·50$ Å^{-1}, *by increments of* 0·01 Å^{-1}

$N = 11$, $L = 5·8$, $l = 1·410$; class 1

11·158	10·951	10·617	10·166	9·616	8·987	8·301	7·580	6·846	6·120
5·421	4·763	4·159	3·617	3·139	2·728	2·381	2·093	1·858	1·668
1·515	1·392	1·291	1·205	1·131	1·064	1·001	0·942	0·886	0·835
0·788	0·747	0·713	0·688	0·672	0·666	0·669	0·680	0·699	0·725
0·754	0·786	0·818	0·849	0·877	0·901	0·919	0·931	0·936	0·936
0·929	0·917	0·900	0·879	0·855	0·829	0·801	0·772	0·743	0·715
0·687	0·662	0·638	0·618	0·602	0·591	0·586	0·589	0·601	0·622
0·653	0·694	0·744	0·804	0·872	0·945	1·023	1·102	1·180	1·255
1·323	1·384	1·435	1·475	1·503	1·519	1·524	1·518	1·503	1·479
1·449	1·414	1·376	1·336	1·296	1·256	1·216	1·179	1·142	1·107
1·073	1·041	1·009	0·978	0·949	0·920	0·892	0·865	0·841	0·819
0·800	0·784	0·773	0·765	0·761	0·761	0·765	0·772	0·781	0·793
0·805	0·817	0·830	0·841	0·851	0·860	0·868	0·875	0·882	0·890
0·898	0·908	0·920	0·934	0·950	0·969	0·989	1·010	1·030	1·050
1·067	1·082	1·092	1·098	1·099	1·095	1·087	1·075	1·061	1·045

$N = 22$, $L = 8·4$, $l = 1·4174$; class 3

22·521	21·637	20·244	18·454	16·402	14·232	12·079	10·058	8·254	6·716
5·461	4·476	3·728	3·174	2·766	2·459	2·219	2·019	1·843	1·682
1·534	1·400	1·279	1·174	1·083	1·006	0·941	0·885	0·836	0·793
0·753	0·714	0·677	0·643	0·612	0·586	0·570	0·567	0·578	0·606
0·651	0·710	0·778	0·850	0·920	0·980	1·026	1·053	1·062	1·052
1·027	0·989	0·944	0·895	0·845	0·798	0·755	0·717	0·683	0·655
0·632	0·612	0·596	0·583	0·570	0·558	0·546	0·535	0·526	0·523
0·530	0·551	0·591	0·654	0·739	0·848	0·974	1·113	1·254	1·390
1·509	1·606	1·673	1·709	1·715	1·695	1·655	1·601	1·541	1·482
1·428	1·381	1·342	1·309	1·280	1·252	1·222	1·189	1·152	1·112
1·069	1·025	0·983	0·944	0·909	0·879	0·852	0·828	0·807	0·786
0·767	0·748	0·732	0·718	0·709	0·705	0·709	0·720	0·739	0·764
0·793	0·824	0·854	0·880	0·900	0·912	0·915	0·910	0·899	0·884
0·869	0·858	0·856	0·863	0·883	0·914	0·956	1·004	1·055	1·104
1·146	1·177	1·196	1·200	1·191	1·169	1·137	1·099	1·058	1·018

$N = 32$, $L = 10$, $l = 1·4174$; class 5

31·717	29·985	27·316	23·998	20·361	16·730	13·376	10·485	8·149	6·371
5·089	4·197	3·583	3·144	2·803	2·513	2·252	2·014	1·803	1·623
1·474	1·353	1·252	1·165	1·085	1·010	0·939	0·873	0·816	0·768
0·729	0·697	0·667	0·637	0·606	0·574	0·545	0·526	0·522	0·541
0·584	0·651	0·737	0·833	0·930	1·017	1·083	1·123	1·135	1·120
1·082	1·029	0·966	0·902	0·840	0·785	0·738	0·700	0·668	0·641
0·619	0·599	0·581	0·565	0·552	0·541	0·531	0·522	0·513	0·505
0·500	0·503	0·522	0·565	0·638	0·747	0·891	1·063	1·251	1·436
1·602	1·732	1·815	1·845	1·827	1·771	1·691	1·602	1·518	1·448
1·396	1·362	1·340	1·323	1·305	1·280	1·248	1·207	1·161	1·111
1·062	1·015	0·973	0·935	0·901	0·871	0·844	0·820	0·798	0·777
0·758	0·740	0·722	0·706	0·693	0·684	0·683	0·691	0·709	0·738
0·775	0·817	0·860	0·898	0·927	0·944	0·947	0·937	0·916	0·888
0·857	0·833	0·817	0·816	0·833	0·869	0·922	0·988	1·060	1·130
1·190	1·233	1·255	1·255	1·234	1·198	1·151	1·100	1·049	1·003

Table 3 (*cont.*)

$N = 72$, $L = 15$, $l = 1{\cdot}4174$; class 7

69·1449	60·7404	49·1248	36·8816	26·1491	18·0540	12·6691	9·3833	7·3958	6·0756
5·0783	4·2788	3·6459	3·1568	2·7742	2·4602	2·1910	1·9575	1·7577	1·5893
1·4476	1·3266	1·2210	1·1274	1·0443	0·9708	0·9058	0·8469	0·7924	0·7425
0·6987	0·6621	0·6315	0·6036	0·5764	0·5507	0·5285	0·5101	0·4937	0·4797
0·4772	0·5045	0·5817	0·7167	0·8958	1·0840	1·2387	1·3263	1·3348	1·2753
1·1742	1·0609	0·9578	0·8751	0·8124	0·7634	0·7218	0·6845	0·6514	0·6228
0·5979	0·5749	0·5530	0·5332	0·5312	0·5044	0·4937	0·4831	0·4730	0·4667
0·4888	0·4719	0·4773	0·4814	0·4941	0·5403	0·6530	0·8567	1·1494	1·4932
1·8229	2·0685	2·1828	2·1586	2·0286	1·8471	1·6670	1·5220	1·4236	1·3680
1·3456	1·3466	1·3602	1·3730	1·3713	1·3456	1·2959	1·2304	1·1609	1·0967
1·0416	0·9950	0·9558	0·9195	0·8880	0·8594	0·8328	0·8078	0·7845	0·7631
0·7433	0·7248	0·7075	0·6921	0·6784	0·6668	0·6556	0·6474	0·6486	0·6682
0·7175	0·7837	0·8680	0·9482	1·0060	1·0296	1·0180	0·9798	0·9287	0·8779
0·8356	0·8034	0·7789	0·7603	0·7518	0·7643	0·8119	0·9028	1·0313	1·1757
1·3046	1·3885	1·4116	1·3772	1·3040	1·2166	1·1349	1·0685	1·0173	0·9770

$N = 128$, $L = 20$, $l = 1{\cdot}4174$; class 9

119·0316	95·0704	66·1014	41·2694	24·8580	16·0667	11·7890	9·3740	7·5891	6·1552
5·0554	4·2419	3·6349	3·1608	2·7666	2·4299	2·1518	1·9310	1·7497	1·5875
1·4394	1·3117	1·2060	1·1154	1·0322	0·9553	0·8873	0·8296	0·7793	0·7325
0·6884	0·6486	0·6143	0·5843	0·5561	0·5298	0·5073	0·4912	0·4815	0·4736
0·4616	0·4521	0·4785	0·5908	0·8142	1·1083	1·3733	1·5105	1·4868	1·3488
1·1778	1·0340	0·9331	0·8621	0·8052	0·7558	0·7132	0·6761	0·6427	0·6125
0·5867	0·5652	0·5460	0·5268	0·5080	0·4920	0·4791	0·4700	0·4602	0·4502
0·4450	0·4460	0·4490	0·4560	0·4630	0·4752	0·5079	0·6443	0·9605	1·4523
1·9915	2·3840	2·4979	2·3496	2·0722	1·8063	1·6164	1·4921	1·4018	1·3347
1·3029	1·3175	1·3669	1·4184	1·4338	1·3953	1·3152	1·2229	1·1427	1·0815
1·0331	0·9918	0·9527	0·9157	0·8824	0·8535	0·8272	0·8015	0·7769	0·7548
0·7356	0·7177	0·6999	0·6829	0·6686	0·6577	0·6489	0·6394	0·6288	0·6266
0·6539	0·7304	0·8535	0·9884	1·0845	1·1081	1·0638	0·9857	0·9105	0·8555
0·8189	0·7927	0·7722	0·7552	0·7382	0·7245	0·7358	0·8092	0·9684	1·1904
1·4040	1·5294	1·5311	1·4358	1·3046	1·1892	1·1082	1·0538	1·0114	0·9725

$N = 288$, $L = 30$, $l = 1{\cdot}405$; class 11

244·4134	150·5266	73·4239	36·8548	23·9653	17·4674	12·8000	9·7153	7·7458	6·3080
5·1877	4·3695	3·7839	3·2360	2·8034	2·5063	2·2122	1·9403	1·7483	1·5944
1·4440	1·2992	1·1837	1·1036	1·0201	0·9306	0·8667	0·8163	0·7573	0·7021
0·6666	0·6374	0·5888	0·5448	0·5392	0·5318	0·4887	0·4563	0·4576	0·4497
0·4315	0·4309	0·4484	0·4491	0·5222	0·8661	1·4241	1·7946	1·7433	1·4704
1·2343	1·0797	0·9746	0·9054	0·8437	0·7763	0·7236	0·6891	0·6529	0·6139
0·5859	0·5636	0·5350	0·5078	0·4929	0·4815	0·4604	0·4392	0·4337	0·4332
0·4192	0·4046	0·4065	0·4111	0·4076	0·4154	0·4485	0·4719	0·4970	0·7586
1·5089	2·4798	2·9945	2·8003	2·3086	1·9413	1·7410	1·6023	1·4826	1·3837
1·3038	1·2465	1·2581	1·3764	1·5166	1·5353	1·4224	1·2870	1·1957	1·1298
1·0711	1·0193	0·9787	0·9356	0·9026	0·8695	0·8393	0·8120	0·7839	0·7636
0·7459	0·7173	0·6959	0·6885	0·6610	0·6522	0·6441	0·6245	0·6093	0·6156
0·6122	0·5978	0·6251	0·7730	0·9830	1·1965	1·2152	1·0980	0·9615	0·8877
0·8489	0·8031	0·7838	0·7626	0·7143	0·7061	0·7280	0·6994	0·6399	0·7779
1·1276	1·4629	1·6634	1·7046	1·5466	1·2815	1·1279	1·1261	1·1035	1·0297

obtained when a constant mean bond length was employed. These comparisons showed that no significant error is introduced by treating such molecules as fragments of a regular lattice, despite the fact that in pyrene the bond lengths vary between 1·39 Å and 1·45 Å, and in coronene between 1·385 Å and 1·43 Å. The errors in intensity that were introduced were less than 0·01 atomic units for $0{\cdot}7 < s < 1{\cdot}1$ Å^{-1} and less than 0·02 atomic units for $0{\cdot}3 < s < 0{\cdot}7$ Å^{-1} in the case of pyrene; whilst in the case of coronene, the curves were indistinguishable in the region $0{\cdot}7 < s < 1{\cdot}0$ Å^{-1}, though a difference of 0·013 atomic units was found at $s = 1{\cdot}15$ Å^{-1} and of 0·020 atomic units at the top of the (10) peak ($s = 0{\cdot}49$ Å^{-1}), where the values for the irregular molecule are actually higher.

A technique whereby a linear combination of such theoretical curves may be fitted to any given observed curve by the method of least squares, thus yielding a layer size distribution, is to be the subject of a second paper.

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The Reduction of Oxide Films by Atomic Hydrogen

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The reactions of atomic hydrogen with thin films of oxides of copper, iron, lead and nickel were investigated, using electron diffraction to determine the crystalline state and composition of the film before and after the action of the atomic hydrogen.

No reduction was observed in the case of iron and nickel oxides, whilst complete reduction was observed with the copper and lead oxides investigated. The crystalline state of the metal after reduction was found to depend on the concentration of the atomic hydrogen, i.e. upon the speed of the reaction.

1. Introduction

The reactions of atomic hydrogen have been studied in detail by Bonhoeffer (1924), Kroepelin & Vogel (1936), and others. These and other previous workers in the field, however, had only optical methods available to identify the reaction products.

In the present experiments the use of electron diffraction has made possible a more critical analysis of the reaction products, and in particular has yielded information on the crystalline state of the products as well as that of the oxide being reduced.

2. Experimental details

The atomic hydrogen was produced by a condensed discharge between aluminium electrodes in the vessel in which the reduction was to take place. The reaction vessel was in the first instance a 6 in. diameter glass sphere with four ground joints, two holding the electrodes, one for the admission of the specimen, and one holding a glass screen which protected the specimen from sputtered aluminium.

In later experiments, however, the electron diffraction camera, in which approximately 60 kV. electrons were used, at camera lengths of 34·5 or 23 cm., was itself used as the reaction vessel to avoid transference of the reduction products through air to the electron diffraction camera with consequent risk of rapid reoxidation. The aluminium electrodes for the production of atomic hydrogen were held inside the camera on tungsten rods led in through glass seals. The electrodes were shielded to prevent the discharge going to the brass walls of the camera.

The hydrogen to be atomized was stored in contact with distilled water to ensure that it contained a certain amount of water vapour (that this was necessary for the production of atomic hydrogen by low and medium-power discharges was shown by Finch (1949)). It was admitted to the apparatus through a long narrow tube to limit its rate of entry, the pressure in the apparatus being kept at about 1 mm. of mercury by means of a rotary pump.

For some experiments hydrogen from a cylinder was purified by passage through the walls of a heated palladium tube before being let into the apparatus, and the apparatus was at the same time kept as dry as possible with phosphorus pentoxide.

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