A Refinement of the Crystal Structure of Ferric Acetylacetonate

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The structure of ferric acetylacetonate has been corrected and refined by the least-squares method with full three-dimensional data (Fe $K\alpha$ radiation). The mean values and standard deviations of chemically equivalent bond lengths are, Fe–O 1·992 (0·006) Å, O–C 1·258 (0·012) Å, C═══C 1·377 (0·019) Å, C–C 1·530 (0·021) Å. Each radical is essentially planar and to a rough approximation they appear to vibrate as rigid bodies.

Introduction

The crystal structure of ferric acetylacetonate was determined by Roof (1956) but as he used only $hk0$ and $hk1$ reflexions it was felt that the z coordinates, and hence the bond lengths, would not be accurate. In connexion with some work on a complex of iron and dextran it was desirable to obtain an accurate value of the length of the iron–oxygen bond in iron-organic compounds, and as ferric acetylacetonate contains six bonds of this type which are all equivalent it was thought to be ideal for this purpose. Consequently a three-dimensional refinement by least-squares methods was undertaken.

Experimental

Dr Roof very kindly sent us some of his original crystals, but some fresh ones were prepared in the way described by him and recrystallized from benzene. Better crystals were obtained in this way than by recrystallization from ether. The space group and lattice constants determined by Roof were confirmed from Weissenberg photographs calibrated with a superimposed rock salt powder picture. The orthorhombic unit cell has the following dimensions:

$$a = 15 \cdot 471; \quad b = 13 \cdot 577; \quad c = 16 \cdot 565 \text{ Å}$$

The space group is *Pbca*. Selected crystals were cut into small blocks of roughly spherical shape and of approximately 0·3 mm diameter and mounted about the a, b and c unit-cell axes and about a face-diagonal axis.

Three-dimensional intensity data were collected from equi-inclination Weissenberg photographs – using multi-film packs and Fe $K\alpha$ radiation. A Leeds–Cox Weissenberg camera fitted with a unidirectional integrating device was used. The densities of the spots were measured with a Joyce–Loebl recording microdensitometer, except for the very weak ones, which were estimated visually. The layer lines recorded were $0kl$, $1kl$, $2kl$, $3kl$, $4kl$, $5kl$; $h0l$, $h1l$, $h2l$, $h3l$, $h4l$ and $h5l$; $hk0$, $hk1$, and $hk2$. In addition, the zero, first and second layers of the b–c diagonal were recorded and these were especially useful in correlating data from all the different layers. The number of reflexions which are theoretically observable with the use of Fe $K\alpha$ radiation is 1840, and intensities were obtained for 1002. The intensities were converted to structure amplitudes by correcting for Lorentz and polarization factors in the usual way. No absorption corrections were applied. The structure factors were placed on the approximate absolute scale by comparison with the calculated values published by Roof.

Refinement of the structure

The refinement was commenced with a least-squares program written by Dr J. C. Schoone for the Stantec Zebra computer, which refines only isotropic temperature parameters. Firstly, a structure-factor calculation was carried out with Roof's published coordinates and the full three-dimensional data and this gave a value of 0·45 for R ($= \Sigma \,||F_o| - |F_c||/\Sigma \,|F_o|$).

To speed up the refinement using the small, rather slow, computer the full three-dimensional data were split into three groups. Group 2 contained all reflexions for which sin $\theta \le 0 \cdot 75$ and for which $|F_o|_{abs} \ge 10 \cdot 0$, and contained 518 planes. Group 1 was the same as group 2 with the omission of planes for which $l > 6$, and this comprised 336 planes. Group 3 comprised the full three-dimensional data.

The atomic scattering factors used for these calculations were, for the carbon and oxygen atoms those given by Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955), for hydrogen that given by McWeeny (1951), and for iron that given by Freeman & Wood (1959). The Fe scattering factor was corrected by a term to allow for the dispersion of the electrons in the K shell as iron radiation was used (James, 1948).

The refinement was commenced with only group 1 reflexions and a mean isotropic temperature parameter was applied to all atoms. Three cycles of coordinate refinement were carried out and this resulted in a drop in R from 0·39 to 0·29 for this group of reflexions. It was noted that the greatest shifts in coordinates were in the z direction as had been expected. The mean temperature parameter and the coordinates were then refined and R fell to 0·22. The refinement was then

continued using group 2 reflexions and, after starting at 0·25, R fell to 0·22 in three cycles. It was felt that the slowness of refinement indicated that there was something wrong and so a calculation of the bond lengths was made. This gave values in good agreement with the expected lengths for all bonds with the exception of O(3)–C(4) (0·963 Å) and C(4)–C(5) (1·762 Å) (Fig. 1). It was clear that atom C(4) was in an incorrect position and a new position for this atom was worked out graphically, using the values for the bond lengths calculated for the other two acetylacetonate radicals. Group 3 reflexions (*i.e.* full 3-D data) were now introduced into a structure factor calculation, and this gave an R value of 0·21, indicating that the movement of C(4) had been correct. Three cycles of refinement were carried out, still with a mean isotropic temperature parameter, and R fell to 0·184. Then a different weighting scheme was introduced. Up to this point each structure factor had been given unitary weight but now the weighting function

$$w^{\frac{1}{2}} = \left[\frac{P}{P + (F_o - Q)^2} \right]^{\frac{1}{2}}$$

was used with P and Q chosen so that unit weight was given to $|F_o| = 5$ and a weight of 0·1 given to $|F_o| = 100$. These figures were arrived at after a consideration of the probable accuracy of the observed structure factors. Further cycles of refinement were then carried out, refining coordinates and individual isotropic temperature parameters for each atom. The value of R fell to 0·154.

Before continuing with the refinement it was felt necessary to introduce the 21 hydrogen atoms in the molecule into the structure factor calculation. A three-dimensional difference synthesis was computed and it was found possible to locate all the hydrogen atoms. It was not always possible to determine the coordinates very accurately and the distance of a hydrogen atom from the carbon atom to which it was attached was adjusted to 1·08 Å. Further cycles of least-squares refinement were performed and R fell to 0·102.

The refinement was then continued on a Ferranti Mercury computer using the least-squares program written by Dr J. Rollett which refined anisotropic temperature parameters. Eight cycles of refinement were carried out, refining the coordinates and anisotropic temperature parameters of all the atoms except the hydrogen atoms. At the end of this, R had fallen to 0·079. The final parameter shifts were very small, so the refinement was concluded. The final observed and calculated structure factors are available from the authors on request
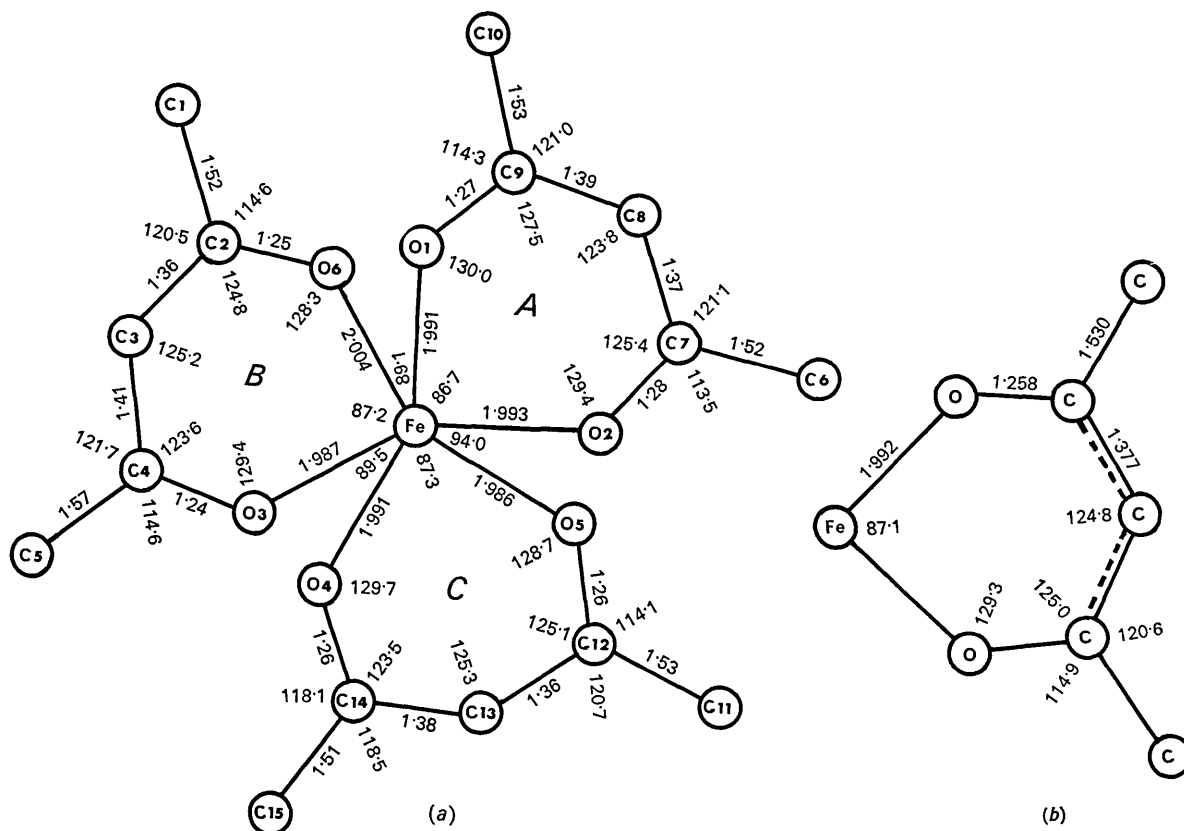

Fig. 1. Ferric acetylacetonate, bond lengths (Å) and angles (°). (a) Complete molecule. (b) Mean values for chemically equivalent bonds and angles.

Discussion

The final fractional atomic coordinates and the standard deviations (in Å) are given in Table 1, and the anisotropic temperature parameters are given in Table 2. When the coordinates in Table 1 are compared with Roof's values, it is clear that the refinement has produced significant changes. Many of the atoms have moved a considerable distance; the greatest movement (0·64 Å) is that of atom C(3) along the y axis. The whole of each radical appears to have moved bodily in one direction, so that the bond lengths and angles obtained will not be very different from those obtained by Roof. The bond lengths obtained are shown in Table 3, and Roof's values are included for comparison and similarly in Table 4 which gives bond angles (see also Fig. 1). As this molecule contains groups of bonds and angles which are chemically equivalent it is possible to calculate a mean numerical value and its standard deviation for each group and these values are included in Tables 3 and 4.

The mean length found for the iron–oxygen bond (1·99 Å) is significantly different from that quoted by Roof (1·95 Å) and is in better agreement with the values found for Co–O (2·05 Å) and Ni–O (2·00 Å) in their respective acetylacetonates (Bullen, 1959, 1961). The new value suggests that the Fe–O bond is much more ionic than covalent which is in direct contrast to the conclusion in Roof's paper.

The angles calculated from the final coordinates confirm the octahedral character of the arrangement of the acetylacetonate radicals about the central iron atom.

The mean plane of each acetylacetonate radical was calculated by the method of Schomaker, Waser, Marsh & Bergman (1959), and the results are given in Table 5. It will be seen that the deviations from these planes are very small in each case.

It is of interest to calculate the vibration–libration tensors for each ring on the assumption that they are pivoting on the iron atom, each as an independent rigid body. Table 6 gives the observed values of U_{ij}

Table 1. *Final atomic coordinates and standard deviations*(Å)

Atom	x/a	σ(x)	y/b	σ(y)	z/c	σ(z)
Fe	0·14272	0·0016	0·26897	0·0015	0·24560	0·0016
O(1)	0·0449	0·006	0·1740	0·006	0·2504	0·008
O(2)	0·0746	0·007	0·3528	0·006	0·3212	0·006
O(3)	0·0949	0·007	0·3392	0·007	0·1503	0·006
O(4)	0·2377	0·007	0·3677	0·006	0·2516	0·008
O(5)	0·2026	0·007	0·1964	0·007	0·3334	0·006
O(6)	0·2027	0·007	0·1794	0·007	0·1674	0·006
C(1)	0·2405	0·015	0·0878	0·014	0·0533	0·014
C(2)	0·1904	0·011	0·1711	0·009	0·0933	0·010
C(3)	0·1388	0·013	0·2308	0·012	0·0488	0·010
C(4)	0·0955	0·010	0·3146	0·011	0·0781	0·010
C(5)	0·0487	0·016	0·3888	0·015	0·0199	0·013
C(6)	−0·0282	0·014	0·4175	0·013	0·4102	0·013
C(7)	0·0007	0·012	0·3368	0·011	0·3528	0·010
C(8)	−0·0498	0·011	0·2562	0·011	0·3386	0·011
C(9)	−0·0256	0·010	0·1786	0·010	0·2892	0·011
C(10)	−0·0843	0·011	0·0890	0·012	0·2781	0·014
C(11)	0·3051	0·015	0·1351	0·015	0·4242	0·015
C(12)	0·2754	0·011	0·2132	0·011	0·3641	0·010
C(13)	0·3245	0·012	0·2946	0·012	0·3495	0·012
C(14)	0·3041	0·011	0·3689	0·009	0·2957	0·012
C(15)	0·3633	0·015	0·4572	0·013	0·2904	0·016
H(1)	0·1982		0·1007		0·0064	
H(2)	0·2327		0·0173		0·0783	
H(3)	0·3036		0·0976		0·0408	
H(4)	0·1799		0·2481		0·0028	
H(5)	0·1027		0·4051		−0·0140	
H(6)	0·0419		0·3146		0·0046	
H(7)	−0·0080		0·3502		0·0250	
H(8)	−0·0341		0·3978		0·4681	
H(9)	−0·0892		0·4475		0·3919	
H(10)	0·0182		0·4683		0·3997	
H(11)	0·8953		0·2415		0·3713	
H(12)	0·8549		0·1107		0·2984	
H(13)	0·9229		0·0383		0·3228	
H(14)	0·8656		0·1393		0·2724	
H(15)	0·3570		0·1632		0·4598	
H(16)	0·3198		0·0797		0·3929	
H(17)	0·2556		0·1229		0·4671	
H(18)	0·3796		0·3043		0·3827	
H(19)	0·3583		0·4752		0·3508	
H(20)	0·4173		0·4289		0·2664	
H(21)	0·3461		0·5119		0·2505	

Table 2. *Final temperature parameters*

$$[2 - (h^2b_{11} + k^2b_{22} + l^2b_{33} + klb_{23} + hlb_{13} + hkb_{12})]$$

	b_{11}	b_{22}	b_{33}	b_{21}	b_{13}	b_{32}
Fe	0·0058	0·0064	0·0042	0·0010	−0·0002	−0·0004
O(1)	0·0063	0·0070	0·0080	−0·0017	−0·0012	−0·0026
O(2)	0·0066	0·0064	0·0055	0·0011	0·0023	−0·0029
O(3)	0·0091	0·0087	0·0038	0·0065	−0·0019	−0·0006
O(4)	0·0064	0·0074	0·0073	−0·0005	0·0008	0·0052
O(5)	0·0083	0·0065	0·0045	0·0000	0·0009	0·0026
O(6)	0·0073	0·0072	0·0054	0·0025	0·0028	−0·0023
C(1)	0·0110	0·0123	0·0104	0·0031	0·0007	−0·0086
C(2)	0·0078	0·0053	0·0053	0·0024	0·0012	−0·0041
C(3)	0·0118	0·0134	0·0043	0·0016	0·0013	−0·0025
C(4)	0·0071	0·0086	0·0047	0·0013	−0·0045	0·0031
C(5)	0·0144	0·0172	0·0074	0·0044	−0·0036	0·0088
C(6)	0·0123	0·0119	0·0092	0·0023	0·0123	−0·0058
C(7)	0·0098	0·0090	0·0048	0·0059	0·0049	0·0019
C(8)	0·0074	0·0082	0·0076	0·0004	0·0065	−0·0000
C(9)	0·0069	0·0070	0·0068	0·0001	0·0008	0·0041
C(10)	0·0059	0·0084	0·0134	−0·0005	−0·0002	0·0012
C(11)	0·0124	0·0171	0·0103	0·0017	−0·0088	0·0111
C(12)	0·0071	0·0092	0·0053	0·0003	−0·0049	0·0015
C(13)	0·0075	0·0115	0·0084	−0·0030	−0·0086	0·0005
C(14)	0·0069	0·0047	0·0082	0·0001	−0·0001	0·0004
C(15)	0·0124	0·0083	0·0126	−0·0068	0·0033	−0·0042

(The hydrogen atoms, in the final cycles of refinement, were given the same temperature parameters as the carbon atoms to which they are attached.)

Table 3. *Bond lengths* (Å)

L(IM): this work, L(R): Roof's values
The chemically equivalent bonds are grouped together and their means are given.

Bond	L(IM)	L(R)		L(IM)	L(R)
Fe–O(1)	1·991	1·979	O(1)–C(9)	1·267	1·105
Fe–O(2)	1·993	1·928	O(2)–C(7)	1·276	1·294
Fe–O(3)	1·987	1·952	O(3)–C(4)	1·242	1·251
Fe–O(4)	1·991	1·921	O(4)–C(14)	1·261	1·134
Fe–O(5)	1·986	1·942	O(5)–C(12)	1·256	1·295
Fe–O(6)	2·004	1·965	O(6)–C(2)	1·248	1·256
Mean	1·992	1·948	Mean	1·258	1·223
Standard deviation	0·006	0·022	Standard deviation	0·012	0·082
C(2)—C(3)	1·355	1·380	C(1)—C(2)	1·522	1·529
C(3)—C(4)	1·408	1·392	C(4)—C(5)	1·571	1·493
C(7)—C(8)	1·366	1·571	C(6)—C(7)	1·519	1·467
C(8)—C(9)	1·386	1·338	C(9)—C(10)	1·529	1·524
C(12)–C(13)	1·363	1·583	C(11)–C(12)	1·525	1·542
C(13)–C(14)	1·384	1·319	C(14)–C(15)	1·512	1·638
Mean	1·377	1·431	Mean	1·530	1·532
Standard deviation	0·019	0·117	Standard deviation	0·021	0·059

Table 4. *Bond angles* (°)

IM: this work, R: Roof's values.
The chemically equivalent angles are grouped together and their means are given.

Angle	IM	R	Angle	IM	R
O(1)–Fe–O(2)	86·7	87·9	C(7)—C(8)—C(9)	123·8	136·3
O(3)–Fe–O(6)	87·2	89·4	C(12)–C(13)–C(14)	125·3	129·5
O(4)–Fe–O(5)	87·3	90·8	C(2)—C(3)—C(4)	125·2	123·6
Mean	87·1	89·4	Mean	124·8	129·8
s.d.	0·32	1·5	s.d.	0·84	6·4
Fe–O(1)–C(9)	130·0	136·7	O(1)–C(9)—C(8)	127·5	114·3
Fe–O(2)–C(7)	129·4	133·5	O(2)–C(7)—C(8)	125·4	107·2
Fe–O(3)–C(4)	129·4	128·8	O(3)–C(4)—C(3)	123·6	124·0
Fe–O(6)–C(2)	128·3	126·7	O(6)–C(2)—C(3)	124·8	117·3
Fe–O(4)–C(14)	129·7	132·3	O(4)–C(14)–C(13)	123·5	120·9
Fe–O(5)–C(12)	128·7	128·7	O(5)–C(12)–C(13)	125·1	111·5

Table 4 (cont.)

Angle	IM	R	Angle	IM	R
Mean	129·3	131·1	Mean	125·0	116·0
s.d.	0·64	3·8	s.d.	1·46	6·4
O(1)–C(9)—C(10)	114·3	121·9	C(8)—C(7)—C(6)	121·1	132·8
O(2)–C(7)—C(6)	113·5	115·2	C(8)—C(9)—C(10)	121·0	123·6
O(3)–C(4)—C(5)	114·6	109·9	C(3)—C(4)—C(5)	121·7	125·2
O(6)–C(2)—C(1)	114·6	107·3	C(3)—C(2)—C(1)	120·5	128·5
O(4)–C(14)–C(15)	118·1	114·4	C(13)–C(12)–C(11)	120·7	123·6
O(5)–C(12)–C(11)	114·1	115·9	C(13)–C(14)–C(15)	118·5	126·7
Mean	114·9	114·1	Mean	120·6	127·1
s.d.	1·64	5·1	s.d.	1·1	4·2

(The following angles are those between the octahedral bonds of the Fe atom)

	IM	R		IM	R
O(1)–Fe–O(6)	89·1	90·3	O(1)–Fe–O(4)	174·5	178·5
O(1)–Fe–O(3)	93·4	88·0	O(2)–Fe–O(6)	175·6	178·2
O(1)–Fe–O(5)	90·2	90·3	O(3)–Fe–O(5)	173·5	177·9
O(2)–Fe–O(3)	91·6	90·3	Mean	174·5	178·3
O(2)–Fe–O(4)	88·5	91·0	s.d.	1·05	0·4
O(2)–Fe–O(5)	94·0	90·8			
O(4)–Fe–O(6)	95·7	90·8			
O(5)–Fe–O(6)	87·5	89·5			
O(3)–Fe–O(4)	89·5	91·0			
Mean	91·1	90·2			
s.d.	2·79	0·3			

Table 5. Deviations from mean plane of each ring

	Ring A		Ring B		Ring C
Fe	+0·009 Å	Fe	−0·065 Å	Fe	−0·022Å
O(1)	+0·003	O(3)	+0·042	O(4)	−0·036
O(2)	−0·012	O(6)	+0·096	O(5)	+0·084
C(6)	+0·025	C(1)	+0·020	C(11)	−0·029
C(7)	−0·009	C(2)	−0·008	C(12)	−0·002
C(8)	−0·026	C(3)	−0·111	C(13)	−0·021

Table 5 (cont.)

	Ring A		Ring B		Ring C
C(9)	−0·007	C(4)	−0·034	C(14)	−0·017
C(10)	+0·016	C(5)	+0·060	C(15)	+0·044

Equations of mean planes

Ring A $0\cdot4377x - 0\cdot4618y + 0\cdot7715z - 2\cdot4097 = 0$
Ring B $0\cdot8069x + 0\cdot5832y - 0\cdot0936z - 3\cdot5953 = 0$
Ring C $-0\cdot4994x + 0\cdot4838y + 0\cdot7187z - 3\cdot6098 = 0$

Table 6. Molecular vibration–libration parameters ($Å^2 \times 10^{-2}$)

	U_{11}		U_{22}		U_{33}		U_{23}		U_{13}		U_{12}	
Ring A	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
Fe	4·81	4·82	4·12	3·51	4·12	4·65	−0·02	−0·08	−0·09	0·23	0·45	0·79
O(1)	6·24	5·51	4·09	4·35	7·19	6·27	−0·25	−0·10	1·12	0·75	−0·78	0·03
O(2)	4·74	5·08	3·79	4·35	6·44	5·39	−0·39	−0·66	−0·17	−0·70	1·05	1·33
C(7)	5·82	5·01	7·22	5·97	5·63	7·38	−1·51	−1·20	−1·78	−1·54	2·70	1·56
C(8)	4·07	4·80	6·18	7·11	8·59	7·08	−1·72	−1·99	−0·98	−1·19	0·74	0·54
C(9)	5·57	5·39	6·25	5·96	5·05	6·39	−1·68	−1·37	−0·34	0·34	−0·69	−0·39
C(6)	5·68	6·14	7·30	7·39	13·91	13·78	−1·50	−1·46	−2·35	−2·26	3·40	3·09
C(10)	6·69	6·88	7·12	7·41	9·48	9·47	−2·61	−2·81	2·71	2·48	−1·92	−2·03

r.m.s. deviation 0·85.

Ring B												
Fe	4·00	3·77	4·06	4·23	4·99	5·52	0·21	−0·27	0·12	0·05	−0·08	0·11
O(3)	3·64	4·83	3·98	3·86	9·31	7·98	0·19	0·61	0·45	0·32	0·33	0·46
O(6)	4·94	5·19	4·62	3·86	6·42	5·67	0·37	0·77	0·53	−0·06	−1·57	−0·53
C(2)	4·66	4·99	4·05	5·78	6·38	7·27	1·04	0·60	0·54	0·43	−1·81	−1·57
C(3)	3·95	3·78	8·74	7·51	10·03	8·41	0·36	0·16	−0·26	0·23	−0·67	−0·27
C(4)	4·88	4·53	4·77	5·76	6·40	8·81	0·11	0·50	0·80	−0·06	2·21	1·30
C(1)	9·12	8·44	7·97	8·12	10·13	10·28	−0·13	0·02	1·73	1·51	−3·13	−4·52
C(5)	8·09	7·75	9·09	8·14	13·17	12·88	0·34	0·12	−1·12	−0·70	3·95	4·24

r.m.s. deviation 1·03.

Ring C												
Fe	4·61	4·43	4·39	4·69	4·05	4·46	−0·25	0·44	−0·30	0·33	0·37	0·92
O(4)	6·34	6·69	3·51	3·59	7·33	6·57	0·19	−0·73	1·32	0·64	0·11	0·24
O(5)	6·69	5·02	3·42	3·63	5·39	4·59	0·26	−0·21	−0·65	−0·56	0·65	0·70
C(12)	3·87	4·78	5·67	5·15	7·47	8·76	−0·31	−0·33	−0·83	−0·63	1·20	1·42
C(13)	3·20	4·40	7·68	6·85	10·95	9·78	−1·03	−0·76	−0·90	−0·79	0·10	−0·08
C(14)	6·32	6·31	4·07	5·20	6·34	7·45	−1·82	−1·25	0·68	−0·13	−0·67	−1·28
C(11)	7·43	7·67	8·07	7·32	15·90	15·83	0·50	0·44	0·19	−0·02	3·61	4·11
C(15)	11·46	10·62	7·35	7·75	9·11	9·09	−1·92	−1·96	−0·57	0·11	−3·91	−4·58

r.m.s. deviation 0·88.

for each atom calculated from the observed values of b_{ij} and in addition the calculated U_{ij} assuming rigid-body movements.

The agreement of these calculated U_{ij} with the observed values is quite good in most cases, but more detailed tests tend to show that the rings cannot be regarded as true rigid bodies. These calculations have been carried out on the University of St Andrews IBM 1620 machine with a program written by Dr D. M. Burns and Mr J. T. McMullan and we are most grateful for their help.

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X-ray Measurements of Stacking Faults in Silver-Antimony Alloys

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The Geiger counter X-ray diffractometer has been utilized to record the line profiles from cold-worked silver-base alloys containing pentavalent solute antimony in the primary solid solution range. The deformation-fault probability α and the twin-fault probability β have been obtained from peak shift and peak asymmetry measurements. Peak shifts of the neighbouring pairs 111–200, 200–220 and 220–311 have been considered in the determination of α and a linear dependence of deformation fault probability with increasing solute concentration has been observed. Using Fourier analysis of line profiles, the effective particle sizes $[D_e]_{hkl}$ and root mean square strains $[\langle \varepsilon_l^2 \rangle]_{hkl}^{1/2}$ have been obtained and it has been found that both are anisotropic in nature and vary considerably with increasing solute content. The role of stacking faults in the particle size broadening has been found to be significant and a fair agreement exists in the values of the compound fault probability $(1 \cdot 5\alpha + \beta)$ evaluated by two different methods.

Introduction

During recent years considerable attention has been given to the presence and effects of stacking faults in f.c.c. metals and alloys. Extensive studies have been made in binary alloys based on the solvent metals copper, silver and gold (Warren & Warekois, 1955; Wagner, 1957; Smallman & Westmacott, 1957; Vassamillet, 1961; Davies & Cahn, 1962; Adler & Wagner, 1962; Foley, Cahn & Raynor, 1963; Vassamillet & Massalski, 1964; Wagner & Helion, 1965; Sen Gupta & Quader, 1966; Goswami, Sen Gupta & Quader, 1966) and from these investigations it has been observed that (i) the stacking fault probability α increases rapidly with increasing solute content, (ii) the increase is either linear or roughly parabolic and (iii) the variation of α with composition is primarily determined by the electron/atom ratio, but that for a fixed electron-atom ratio, α increases as the solute valency increases. But these investigations, in general, are concerned with solid solutions of di,- tri-, or tetra-valent solutes in solvent metals copper, silver and gold and measure-

ments with pentavalent solute were lacking. Very recently, Sastry, Rama Rao & Anantharaman (1965) have determined the stacking-fault densities in alloys of silver with pentavalent solute element antimony and observed that the variation of α with electron-atom ratio is similar to the trends observed by Davies & Cahn (1962) for silver- and copper-base alloys.

The present investigation deals with silver-antimony alloys in the primary solid solution range and seeks to give a fairly detailed picture of the deformed state in this system from peak position, peak asymmetry and peak broadening measurements using the conventional methods. This will also form an extension of the previous measurements with di-, tri- and tetra-valent solutes in silver, *i.e.* in solvent of the same period as the solutes.

Experimental results

Sample preparation and experimental procedure

The preparation of alloys from spectrographically standardized silver and antimony supplied by Johnson, Matthey & Co., Ltd, London, follows the same method