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The Fourier transform of the regular octahedron.

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In the course of some research in these Laboratories (Corey *et al.*, 1962) the complex ions $Ta_6Cl_{12}^{++}$ and $Nb_6Cl_{12}^{++}$ have been used to form a pair of isomorphous crystals of the protein lysozyme. In these complex ions the metal atoms are arranged in a regular octahedron with edges of length 2·98 Å (Vaughan *et al.*, 1950). The question arose as to the effect of the orientation of the octahedron upon its Fourier transform. Although Wrinch (1946) has investigated the Fourier transform of an octahedral arrangement of atoms, some additional information is necessary in order to elucidate the effect of orientation.

The purpose of this paper is to present this additional information, namely: the average value, the root mean square value, and the maximum and minimum values of the Fourier transform as a function of the scattering angle.

The transform of six atoms, each with atomic scattering factor f and located at $(a/2, 0, 0)$, $(-a/2, 0, 0)$, $(0, a/2, 0)$, $(0, -a/2, 0)$, $(0, 0, a/2)$, and $(0, 0, -a/2)$, is given by

$$A = 2f\{\cos 2\pi h + \cos 2\pi k + \cos 2\pi l\} .$$

The averaging of this function is carried out on the surface of a sphere in reciprocal space, which imposes the condition that

$$h^2 + k^2 + l^2 = (a \sin \theta/\lambda)^2 = c^2,$$

where h, k, and l are not necessarily integers.

By changing to spherical polar coordinates the expression for the average value of the transform becomes:

$$\bar{A} = 4f/\pi \int_0^{\pi/2}\int_0^{\pi/2} \{\cos(2\pi c \sin\theta\cos\varphi) + \cos(2\pi c \sin\theta \sin\varphi) + \cos(2\pi c \cos\theta)\} \sin\theta d\theta d\varphi .$$

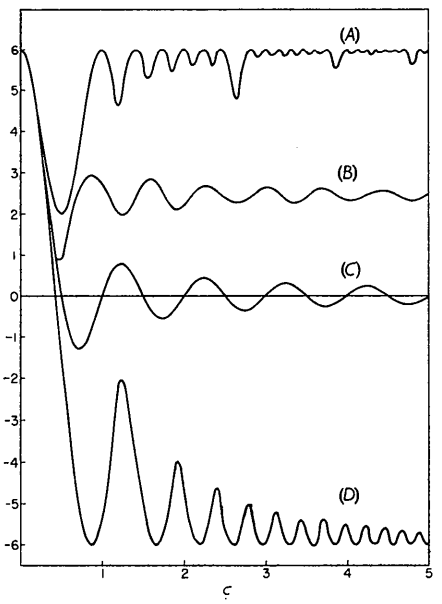

Fig. 1. A plot of the data contained in Table 1 showing the values from special cases of the Fourier transform of an octahedron: curve A, A_{max}/f; curve B, $\sqrt{(\bar{A}^2)}/f$; curve C, $\bar{A}/f$; and curve D, A_{min}/f.

Table 1

(1) c	(2) $\frac{A_{max}}{f}$	(3) $\frac{\sqrt{\bar{A}^2}}{f}$	(4) $\frac{\bar{A}}{f}$	(5) $\frac{A_{min}}{f}$
0.00	6.00	6.000	6.000	6.00
0.05	5.90	5.902	5.902	5.90
0.10	5.62	5.613	5.613	5.61
0.15	5.18	5.150	5.150	5.14
0.20	4.62	4.541	4.541	4.49
0.25	4.00	3.821	3.820	3.70
0.30	3.38	3.031	3.027	2.79
0.35	2.85	2.224	2.207	1.79
0.40	2.38	1.468	1.403	0.71
0.45	2.10	0.916	0.666	-0.35
0.50	2.00	0.891	0.000	-1.44
0.55	2.10	1.294	-0.537	-2.46
0.60	2.38	1.758	-0.935	-3.41
0.65	2.82	2.165	-1.189	-4.25
0.70	3.38	2.481	-1.297	-4.94
0.75	3.99	2.709	-1.275	-5.46
0.80	4.62	2.861	-1.135	-5.85
0.85	5.16	2.916	-0.909	-5.98
0.90	5.62	2.910	-0.624	-5.95
0.95	5.89	2.841	-0.311	-5.72
1.00	6.00	2.718	0.000	-5.30
1.05	5.90	2.552	0.281	-4.72
1.10	5.62	2.360	0.510	-3.97
1.15	5.18	2.173	0.672	-3.10
1.20	4.62	2.026	0.757	-2.11
1.25	4.96	1.963	0.764	-2.06
1.30	5.49	2.005	0.699	-2.47
1.35	5.82	2.141	0.572	-3.07
1.40	5.99	2.331	0.401	-3.77
1.45	5.95	2.528	0.204	-4.44
1.50	5.72	2.691	0.000	-5.07
1.55	5.30	2.795	-0.190	-5.54
1.60	5.32	2.822	-0.351	-5.87
1.65	5.70	2.774	-0.468	-5.99
1.70	5.96	2.668	-0.534	-5.93
1.75	5.99	2.499	-0.546	-5.67
1.80	5.82	2.328	-0.508	-5.24
1.85	5.46	2.186	-0.418	-4.68
1.90	5.62	2.109	-0.296	-4.02
1.95	5.89	2.115	-0.151	-4.07
2.00	6.00	2.194	0.000	-4.79
2.05	5.90	2.314	0.144	-5.34
2.10	5.62	2.444	0.267	-5.75
2.15	5.69	2.555	0.359	-5.95
2.20	5.95	2.630	0.413	-5.98
2.25	5.99	2.663	0.424	-5.80
2.30	5.84	2.656	0.396	-5.44
2.35	5.58	2.615	0.329	-4.91
2.40	5.90	2.551	0.234	-4.62
2.45	6.00	2.475	0.120	-5.17
2.50	5.90	2.400	0.000	-5.63
2.55	5.61	2.335	-0.116	-5.90
2.60	5.14	2.290	-0.215	-6.00
2.65	4.78	2.270	-0.292	-5.89
2.70	5.36	2.279	-0.336	-5.60
2.75	5.74	2.317	-0.347	-5.15
2.80	5.97	2.379	-0.324	-5.06
2.85	5.98	2.454	-0.271	-5.54
2.90	5.89	2.529	-0.194	-5.87
2.95	5.89	2.591	-0.100	-5.98
3.00	6.00	2.627	0.000	-5.93
3.05	5.90	2.628	0.097	-5.67
3.10	5.86	2.594	0.181	-5.24
3.15	5.99	2.527	0.245	-6.36
3.20	5.95	2.440	0.284	-5.76
3.25	5.83	2.351	0.294	-5.97
3.30	5.99	2.282	0.275	-5.98
3.35	5.96	2.250	0.231	-5.80
3.40	5.84	2.264	0.165	-5.43
3.45	5.99	2.319	0.086	-5.45
3.50	5.95	2.400	0.000	-5.81
3.55	5.88	2.485	-0.083	-5.98
3.60	6.00	2.556	-0.156	-5.97
3.65	5.92	2.599	-0.212	-5.76
3.70	5.93	2.608	-0.245	-5.57
3.75	6.00	2.586	-0.255	-5.68
3.80	5.97	2.536	-0.239	-5.93
3.85	5.55	2.474	-0.201	-6.00
3.90	5.62	2.412	-0.144	-5.86
3.95	5.90	2.361	-0.075	-5.54
4.00	6.00	2.332	0.000	-5.67
4.05	5.90	2.326	0.073	-5.93
4.10	5.98	2.341	0.137	-6.00
4.15	5.97	2.373	0.186	-5.87
4.20	5.93	2.414	0.216	-5.56
4.25	6.00	2.458	0.225	-5.75
4.30	5.87	2.498	0.211	-5.96
4.35	6.00	2.530	0.178	-5.99
4.40	5.93	2.550	0.128	-5.81
4.45	5.98	2.554	0.066	-5.58
4.50	5.97	2.540	0.000	-5.88
4.55	5.96	2.510	-0.065	-6.00
4.60	5.99	2.466	-0.122	-5.92
4.65	5.93	2.415	-0.166	-5.65
4.70	6.00	2.367	-0.193	-5.81
4.75	5.86	2.333	-0.201	-5.98
4.80	5.62	2.323	-0.189	-5.96
4.85	5.91	2.340	-0.159	-5.75
4.90	6.00	2.381	-0.115	-5.78
4.95	5.90	2.438	-0.060	-5.98
5.00	6.00	2.497	0.000	-5.98

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Evaluation of this integral leads to:

$$\bar{A} = 6f \sin 2\pi c/(2\pi c) .$$

This is the transform of a spherical shell multiplied by $6f$. The function $\bar{A}/f$ is shown in curve C, Fig. 1, and selected values are listed in column 4, Table 1.

The expression for the mean square value is:

$$\bar{A^2} = 8f^2/\pi \int_0^{\pi/2} \int_0^{\pi/2} \{\cos(2\pi c \sin\theta\cos\varphi) + \cos(2\pi c \sin\theta \sin\varphi) + \cos(2\pi c \cos\theta)\}^2 \sin\theta d\theta d\varphi$$

or

$$\bar{A^2}/f = 8\left\{\frac{3}{4} + \frac{3}{4}\frac{\sin 4\pi c}{4\pi c} + \frac{\sin 2\sqrt{(2)}\pi c}{2\sqrt{(2)}\pi c} + 2\int_0^{\pi/2} \cos(2\pi c \cos\theta) J_0(2\pi c \sin\theta) \sin\theta d\theta\right\} .$$

The integral was evaluated by Simpson's rule. The function $\sqrt{(\bar{A^2})}/f$ is shown in curve B, Fig. 1 and selected values are listed in column 3, Table 1.

Since the function A has many relative maxima and minima, the most feasible method for obtaining the absolute maximum and absolute minimum seemed to be the evaluation of A for many closely spaced values of h and k. These calculations were made and the functions A_{max}/f and A_{min}/f are shown in curves A and D, Fig. 1; selected values are listed in columns 2 and 5, Table 1.

All of the calculations for A/f, $\sqrt{(\bar{A^2})}/f$, A_{max}/f, and A_{min}/f were done on a Burrough's 220 computer. The absolute error in $\bar{A}/f$ and $\sqrt{(\bar{A^2})}/f$ is less than 0·001; the absolute error in A_{max}/f and A_{min}/f is less than 0·01.

Wilson (1942) has shown that for a random distribution of nearly equal atoms

$$\bar{A^2} = \Sigma f_i^2 .$$

If this relation is applied to the present structure, even though the atoms are hardly distributed in a random manner, the expected value of $\sqrt{(\bar{A^2})}/f = \sqrt{6} = 2{\cdot}449$.

From curve B, Fig. 1 and the expression for the root mean square value it is clear that the value $\sqrt{6}$ is approached quite closely, particularly for large values of c. When one applies Wilson's relation, one normally operates in discrete ranges of values of c (or $\sin\theta/\lambda$). Since the number of reflections one may expect for a given value of c is proportional to c^2, a weighted average has been computed over ranges of c using the values, ci, in column 1, Table 1 and the corresponding values $(\sqrt{(\bar{A^2})}/f)_i$, in column 3, Table 1.

The results are given in Table 2.

Table 2. *Average value of* $\sqrt{(\bar{A^2})}/f = \Sigma c_i^2 \sqrt{(\bar{A^2})}/f_i/\Sigma c_i^2$.

Range of c	Average value of $\sqrt{(\bar{A^2})}/f$
0·0–1·0	2·515
1·0–2·0	2·374
2·0–3·0	2·456
3·0–4·0	2·456
4·0–5·0	2·428
0·0–5·0	2·439

These values fall quite close to the predicted value of 2·449.

The diameter of the tantalum and niobium octahedra is 4·21 Å. For reflections out to a minimum spacing of 5 Å, c has a maximum value of 0·421. From Fig. 1 it may be seen that for work at this low resolution the orientation of the complex has little effect on its Fourier transform.

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The structure of the iodine complex of 1,4-selenothiane, $C_4H_8SSe.2I_2$.

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Structural studies of the iodine complexes of 1,4-dithiane (Chao & McCullough, 1960) and of 1,4-diselenane (Chao & McCullough, 1961) have shown that these substances have similar (nearly isomorphous) crystal structures even though their molecular structures are quite different. In the dithiane complex, the iodine molecules are bonded to sulfur atoms in the six-membered ring in equatorial positions while the bonding in the diselenane complex is axial. This immediately raises the question of the configuration of the iodine complex of 1,4-selenothiane which contains one selenium atom and one sulfur atom in the ring. Several possibilities are suggested by analogy, one axial–axial, one equatorial–equatorial and two axial–equatorial configurations. The present study was undertaken in order to answer this question.

The preparation and properties of 1,4-selenothiane and its derivatives will be described elsewhere. Crystals of the iodine complex are garnet-red needles elongated on b. Precession and Weissenberg photographs about the b axis indicated the following unit cell dimensions based on Mo $K\alpha = 0{\cdot}7107$ Å:

$$a = 6{\cdot}80 \pm 0{\cdot}03,\ b = 6{\cdot}38 \pm 0{\cdot}03,$$
$$c = 16{\cdot}69 \pm 0{\cdot}08 \text{ Å};\ \beta = 114{\cdot}1 \pm 0{\cdot}4°.$$

The measured density was found to be 3·33 g.cm.$^{-3}$ while that calculated on the basis of $2(C_4H_8SeSI_4)$ in the unit cell is 3·39 g.cm.$^{-3}$. The only systematic extinctions

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