Mathematical solution

The neglecting of second and higher order terms in the expansion of $|\partial\mathbf{r}_i|$ imposes a limitation on the allowed shifts if the formulation of the problem is to retain its physical meaning. This, of course, is the same restriction as applies to the least-squares technique where unfortunately it is not possible to allow for it. Let

$$\partial\mathbf{r}_i = \partial x_i \mathbf{i} + \partial y_i \mathbf{j} + \partial z_i \mathbf{k} ,$$

where, because of the restriction on the shifts,

$$\varepsilon_{i,1} \geq \partial x_i \geq -\varepsilon_{i,1}$$
$$\varepsilon_{i,2} \geq \partial y_i \geq -\varepsilon_{i,2}$$
$$\varepsilon_{i,3} \geq \partial z_i \geq -\varepsilon_{i,3} .$$

Define new variables,

$$\partial u_i = \partial x_i + \varepsilon_{i,1}$$
$$\partial v_i = \partial y_i + \varepsilon_{i,2}$$
$$\partial w_i = \partial z_i + \varepsilon_{i,3}$$

so that

$$2\varepsilon_{i,1} \geq \partial u_i \geq 0$$
$$2\varepsilon_{i,2} \geq \partial v_i \geq 0$$
$$2\varepsilon_{i,3} \geq \partial w_i \geq 0 .$$

The problem is now one of optimization subject to a set of linear constriction with all variables being positive and was originally solved by Dantzig (1951). It is not necessary to outline the method of solving these inequalities to obtain a minimum in $\Sigma\, w_i \Delta^2_{i,p}$ as there can be few computers for which linear programming programs do not exist, such is its importance in the theory of economics.

It is worth noting that there are numerous strategies for the use of this technique. It is by no means necessary to have one inequality for each structure factor and they could be grouped together to give inequalities for various regions of reciprocal space or for various ranges of intensity, always, of course, treating separately those which had values $w\Delta^2$ which differed appreciably from experimental prediction.

Conclusion

It has been shown that the linear programming technique of minimizing the linearized function $\Sigma\, w_i \Delta^2_i$ has certain advantages to offer in deciding the accuracy of a given structure model over that of the conventional least-squares technique which does not use the maximum information derivable from the data. It is to be expected that for a refined structure using high quality data ($\tau_i(\mathbf{h})$ all small) the two techniques in the limit would give the same minima. It is dubious if this would be true if the $\tau_i(\mathbf{h})$ values are large.

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A Comparison of Experimental X-ray Structure Amplitudes for Sodium Chloride

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Recent X-ray structure amplitude data for sodium chloride are divided into a consistent majority and an inconsistent minority by statistical methods. A set of mean value estimates of the structure amplitudes is derived from the consistent data.

X-ray structure amplitudes (at room temperature) for sodium chloride have been measured many times in recent years (Table 1). Considerable differences occur, so that it is difficult to extract useful information about, say, the electron distribution and thermal motion in this alkali halide. The purpose of the present note is to compare the different experimental results for reflexions with $h^2 + k^2 + l^2 \leq 48$ and to show that these results may be grouped into a consistent majority and an inconsistent minority.

The comparison has been restricted to this range of low-order reflexions for several reasons. Firstly, the range is common to most experiments. Secondly, the experimental measurements of these low-order reflexions are not very sensitive to those differences in experimental techniques which lead to different rates of fall-off, with angle, of the higher order reflexions. Thirdly, accurately known structure amplitudes for this range would provide a great deal of information about the electron distribution. With this in mind, a set of mean value estimates of the structure amplitudes has been derived from the consistent data and is presented in Table 3.

Brief details of the data to be compared are given in Table 1; mosaic single-crystal data published before 1952 have been excluded since, as Renninger (1952)

Table 1. *Some details of room-temperature measurements of X-ray structure amplitudes of sodium chloride*

Authors	Wasastjerna (1946)	Renninger (1952)	Witte & Wölfel (1955)	Schoknecht (1957)	Vihinen (1960)	Abrahams & Bernstein (1965)	
						Crystals 1,3 AB1, AB3	Crystals 4,5 AB4, AB5
Abbreviation	WAS	REN	W & W	SCH	Powders A,B,C,D V-A,B,C,D		
Specimen type	Powder	Mosaic single crystal	Crystal plates Powder plates	Mosaic single crystal	Powder	Mosaic single crystal	Mosaic single crystal
X-radiation	Cu $K\alpha$	Cu $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Cu $K\alpha$	Cu $K\alpha$	Mo $K\alpha$
Corrected for anomalous dispersion?	No	Yes	No	No	Yes	Yes	Yes
Scale	Relative	Absolute	Absolute	Absolute	Relative	Relative	Relative
Special features							

Wasastjerna alone recorded reflexion intensities on photographic film.
Witte & Wölfel used separate methods to determine structure amplitudes for strong, medium and weak reflexions.
Abrahams & Bernstein were primarily interested in determining the accuracy of measurement of an automatic diffractometer, not in providing error-free structure amplitudes.

has shown, these are almost certainly erroneous and likely to underestimate the magnitudes of weak relative to strong reflexions. As Table 1 shows, the published sets of data differ in scale. Some are absolute measurements; others contain a scale factor which may differ slightly from unity. Furthermore, different sets incorporate quite different corrections for anomalous dispersion. The data must therefore be adjusted as closely as possible to a common scale and have consistent corrections for anomalous dispersion made to them before a proper comparison can be performed.

Corrections of the data of Table 1 for anomalous dispersion were made in the following way. Firstly, those corrections which were reported as having been made in the published data were removed,* so that all measurements were then appropriate to the radiation (Cu $K\alpha$ or Mo $K\alpha$) used in the experiments.

The corrections which should now be applied to the experimental measurements, thus restored, were estimated with the aid of a model lattice of Hartree–Fock free ions at the observed lattice spacing. However, these estimates prove to be quite insensitive to the particular model used, as will be shown below. $\Delta f'$, $\Delta f''$ were taken from Cromer (1965) and the B values and scale factor of the model were chosen to minimize the expression

$$\sum_{hkl} \{F_{exp} - F_{model}(k,B)\}^2 \, .$$

Finally, the dispersion contributions to the experimental data were taken to be the differences between the structure amplitudes calculated from the above model and from the corresponding dispersion-free model.

Dispersion corrections obtained in this way for different sets of experimental data agreed with each other to within about 0·02,† and their mean values for different reflexions are given in Table 2. Other models,

Table 2. *Average values of the anomalous dispersion corrections applied to the data of Table* 1

hkl	Cu $K\alpha$	Mo $K\alpha$	hkl	Cu $K\alpha$	Mo $K\alpha$
111	0·23	0·11	⌠ 333	0·20	0·09
200	0·44	0·18	⌡ 511		
220	0·42	0·17	440	0·34	0·14
311	0·23	0·10	531	0·18	0·08
222	0·41	0·17	⌠ 442	0·32	0·14
400	0·39	0·16	⌡ 600		
331	0·21	0·09	620	0·31	0·13
420	0·38	0·15	533	0·17	0·08
422	0·36	0·15	622	0·29	0·13
			444	0·28	0·12

* Renninger gave in his paper a reference to the corrections which he used. Abrahams & Bernstein (private communication) used the values of $\Delta f'$, $\Delta f''$ listed in *International Tables for X-ray Crystallography* (1962). The corrections which they made can be deduced from these values and other information provided in their papers. In the case of Vihinen (1960), uncorrected structure amplitudes can be deduced directly from his Table V.

† The corrections are too small to be affected significantly by small differences in the scales of the experimental data.

Table 3. Structure amplitudes of sodium chloride

The Table lists $\bar{F}$ and σ, defined by equations (1) and (2), and also the departure $\Delta F\ (=kF-\bar{F})$ of individual sets of experimental data from the set of mean values. Numbers in italics relate to a comparison of all sets of data mentioned in Table 1; numbers in ordinary type refer to a comparison which omits the measurements WAS, SCH and AB3. The favoured sets of mean values $\bar{F}$ and standard deviations σ are those in ordinary type.

hkl	k	111	200	220	311	222	400	331	420	422	333,511	440	531	442,600	620	533	622	444	Number of data p	Ratio† r
$100\bar{F}^*$		467	2019	1634	255	1422	1258	237	1113	994	246	831	240	769	711	221	638	602		
$100\bar{F}^*$ (ital.)		466	2038	1627	254	1396	1250	236	1100	975	245	818	236	757	694	219	621	597		
100σ		15	20	29	10	16	24	8	16	8	6	9	5	12	13	4	15	15		
100σ (ital.)		18	59	32	18	43	25	8	18	26	13	24	9	34	32	12	33	33		
$100\Delta F$																				
W & W	1·000	−7	−18	34	−3	3	−29	2	−3	7	9	0	−3	17	18	1	12	6	17	0·44
W & W (ital.)	1·000	−6	−37	41	−2	29	−21	3	10	26	10	13	1	29	35	3	29	11		0·31
REN	0·997	2	17	—	−11	−8	−24	5	—	—	−0	—	—	−1	—	—	−8	1	10	0·21
REN (ital.)	0·995	2	−6	—	−10	15	−19	6	—	—	−0	—	—	9	—	—	8	5		0·16
SCH (ital.)	0·996	26	−15	—	—	−39	−26	11	—	—	30	—	—	55	—	20	—	59	9	1·19
AB4	1·023	−18	—	−53	—	33	53	6	26	−11	2	−9	1	−11	−14	4	−4	−14	16	0·92
AB4 (ital.)	1·011	−22	—	−64	5	42	45	5	26	−3	−0	−5	7	−8	−5	4	6	−16		0·49
AB5	1·040	21	—	2	14	−17	3	11	16	8	−0	9	6	−13	−10	−2	−2	−31	16	0·67
AB5 (ital.)	1·027	16	—	−11	12	−8	−5	10	15	14	−3	12	3	−10	−1	−2	8	−33		0·29
AB1	1·002	29	−36	40	17	13	−5	8	9	5	−0	12	3	−10	6	7	−35	—	16	0·99
AB1 (ital.)	0·995	27	−68	35	17	29	−6	8	15	16	−3	−14	5	−3	19	8	−22	—		0·49
AB3 (ital.)	1·014	17	97	−4	5	−121	51	−6	−4	−56	4	−6	−9	−52	−29	0	−70	—	16	1·09
V–A	0·982	−1	6	−3	−4	−3	2	−10	−12	8	−10	10	−7	−8	−13	4	6	12	17	0·50
V–A (ital.)	0·976	−3	−25	−6	−4	14	2	−10	−6	21	−11	18	−11	−0	1	5	20	13		0·20
V–B	0·985	−5	5	5	−7	−16	−15	−9	−13	−4	−8	7	5	22	12	−5	16	8	17	0·51
V–B (ital.)	0·979	−7	−27	2	−7	1	−15	−9	−7	8	−9	15	8	29	25	−3	29	9		0·25
V–C	0·982	−7	5	−10	−2	3	15	−8	−8	−3	−2	−4	1	−0	−9	−3	1	10	17	0·14
V–C (ital.)	0·976	−8	−26	−12	−2	21	15	−8	−5	10	−3	4	3	7	4	−2	15	11		0·11
V–D	0·982	−12	21	−15	−8	−8	0	−5	−18	−11	4	0	−2	6	11	−5	12	8	17	0·37
V–D (ital.)	0·977	−14	−9	−17	−8	9	1	−5	−12	2	3	9	0	13	24	−4	26	9		0·16
WAS (ital.)	1·017	−29	115	37	−5	−22	−22	−6	−38	−37	−23	−64	−22	−68	−73	−29	−51	−68	17	1·98

* The structure amplitudes $\bar{F}$ have the same scale as the data of Witte & Wölfel.

† $r = \{\Sigma(\Delta F/\sigma)^2\}/\chi^2_p(5\%)$. $\chi^2_p(5\%) = 16{\cdot}9,\ 18{\cdot}3,\ 26{\cdot}3$ and $27{\cdot}6$ for $p=9, 10, 16$ and 17 respectively.

based on neutral atoms and distorted ions, lead to results which agree with those of Table 2 to within 0·01 and it is clear that the use of a model is simply a convenient device for obtaining the dispersion corrections appropriate to the experimental data. Having computed these corrections, *theoretical models do not enter further into the comparison of the results obtained experimentally.*

The sets of dispersion-corrected structure amplitudes, derived by the above procedure, still differ slightly in scale. Scale factors k_i, with k_1 arbitrarily put equal to unity, have been introduced to bring them into as close agreement as possible, in the following sense. Define the mean and variance of the structure amplitude for the jth reflexion to be

$$\bar{F}_j = \frac{1}{n_j} \sum_i k_i F_{ij} \qquad (1)$$

and

$$\sigma_j^2 = \frac{1}{(n_j - 1)} \sum_i (k_i F_{ij} - \bar{F}_j)^2, \qquad (2)$$

where n_j is the number of sets of data for which measurements F_{ij} exist. The k_i were chosen to minimize the quantity $\sum_j \sigma_j^2$ and their values are recorded in Table 3, along with other information discussed below. Use of this simple criterion to determine the k_i receives some *a posteriori* justification in that the calculated k_i are very similar for the three sets of nominally absolute measurements. They are also similar for the four sets of Vihinen, who claimed to have adjusted them to a common scale.

The dispersion-corrected and scale-adjusted sets of data can be compared with the set of mean values $\bar{F}_j$ by means of a χ^2-test. The use of this test may be roughly justified by the following arguments. Since there is a minimum of seven measurements for any one reflexion and since no set of data contains fewer than nine members, effects of small sample size should not be very important. Thus, the estimated quantities $\bar{F}_j$ and σ_j^2 may reasonably de taken to be the true values and, assuming normally distributed errors, the quantity S_i defined by the equation

$$S_i = \sum_j \{(k_i F_{ij} - \bar{F}_j)/\sigma_j\}^2$$

should be distributed like χ^2 with no more than p_i degrees of freedom, where p_i is the number of reflexions in data set i. Values of p_i, $\chi_{p_i}^2(5\%)$ (the value which S_i should exceed with a probability of five per cent) and the ratio $r_i = S_i/\chi_{p_i}^2(5\%)$ are listed in Table 3.

Numbers in italic type in Table 3 relate to a comparison of all of the published data mentioned in Table 1. We see there that r_i exceeds unity [or, equivalently, S_i exceeds $\chi_{p_i}^2(5\%)$] only for the data SCH, WAS and AB3, and we conclude that these three sets differ significantly from $\bar{F}$. It will be noted that the differences of the measurements SCH from $\bar{F}$ are fairly systematic in that they are negative for the three strongest reflexions and positive otherwise. The devia-

tions of WAS from $\bar{F}$ are also systematic and it is interesting to note that these data can be brought into surprisingly close agreement with $\bar{F}$ by a correction which is quadratic in F. This suggests that Wasastjerna might have used an incorrect conversion from photographic film blackening into values of reflexion intensities.

The numbers in ordinary type in Table 3 refer to a comparison which does not include SCH, WAS or AB3. No set of data fails the new χ^2 test, though AB1 and AB4 come close to failure. Inspection of the Table shows that the measurements of Abrahams & Bernstein for the reflexions of lowest order differ erratically and by large amounts from $\bar{F}$. The remaining sets and Wasastjerna's results, suitably modified as above, agree quite well with one another. This suggests that the set of mean values, $\bar{F}$, may be a close approximation to the true structure amplitudes of sodium chloride.

Although $\bar{F}$ is probably correct to 1–2%, structure amplitudes will require to be known to higher accuracy to provide a reliable description of significant features of the electron density in the crystal. The precision of $\bar{F}$ could be improved to a limited extent by the inclusion of further sets of data in an analysis of the above type. Higher accuracy than that gained simply by statistical factors would require improved experimental accuracy, and this necessitates assessment of the factors leading to differences between the sets of data. The recent report of the American Crystallographic Association's single-crystal project (Abrahams, Alexander, Furnas, Hamilton, Ladell, Okaya, Young & Zalkin, 1967) is particularly relevant. Consideration of the measurements of reduced intensities, and especially the comparison of these for secondary crystals with the primary standard crystal, lead to the conclusion that internal perfection of these crystal specimens was a major cause of variation in measured intensities, while differences in experimental set-up caused other but probably less significant deviations.

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