

SHORT COMMUNICATIONS

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A simple statistical treatment of unobserved reflexions. Application to two organic substances. By I. VICKOVIĆ,* *Institute of General and Inorganic Chemistry, the University, Ul. Soc. Revolucije 8, Zagreb, Yugoslavia* and D. VITERBO, *Istituto di Chimica-Fisica, Università, Corso M. D'Azeglio 48, 10125 Torino, Italy*

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Abstract

A simple statistical method for estimating the unobserved reflexions is described together with its application to the solution, by means of direct methods, of the crystal structure of two organic compounds. The method proved to be successful in solving both structures for which more than 60% of the reflexions had not been measured because they were too weak.

It is a common option for most computer-controlled diffractometers to skip the measurement of the very weak reflexions in order to save time in data collection. We recall here that speed in data collection is often required to reduce the extent of radiation damage on sensitive crystals.

When using this option, the number of actually measured reflexions can sometimes be as small as 30–40% of those within the chosen reciprocal lattice sphere. In these cases we can expect that any statistical calculation on the measured intensities will have little meaning and that the application of direct methods to the solution of the structure will be unsuccessful.

A procedure for the treatment of the unobserved reflexions has been described by Hamilton (1955). We have used a similar approach in order to evaluate the non-measured reflexions to be introduced into the direct-method procedures.

(1) The reflexions are divided into shells of $s = \sin \theta/\lambda$.

(2) Within each shell an average intensity $\langle F^2 \rangle$ is evaluated, assigning initially to all the unobserved reflexions the mean value suggested by Hamilton (1955), *i.e.*,

$$P1: \mu \simeq F_{\text{omin}}^2/2 \quad \text{and} \quad P\bar{1}: \mu \simeq F_{\text{omin}}^2/3,$$

where F_{omin}^2 is the local minimum observed intensity.

(3) Considering the centric or acentric distributions (Wilson, 1949) expressed in terms of the normalized intensities, $z = F^2/\langle F^2 \rangle$, the amplitude of each unobserved reflexion is found as a random number, distributed according to the proper distribution, in the range between zero and the local minimum intensity. To all unobserved reflexions within each shell is assigned the same standard deviation computed, according to Hamilton (1955), as

$$P1: \sigma(F) \simeq F_{\text{omin}}/2\sqrt{12} \quad \text{and} \quad P\bar{1}: \sigma(F) \simeq F_{\text{omin}}/\sqrt{45}.$$

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The application of this procedure has proved to be very successful.

As an example we report the results obtained for the structure of 2-phthalimido-4-ethoxy- γ -butyrolactone ($\text{C}_{14}\text{H}_{13}\text{NO}_5$) (LAKAT), belonging to the space group

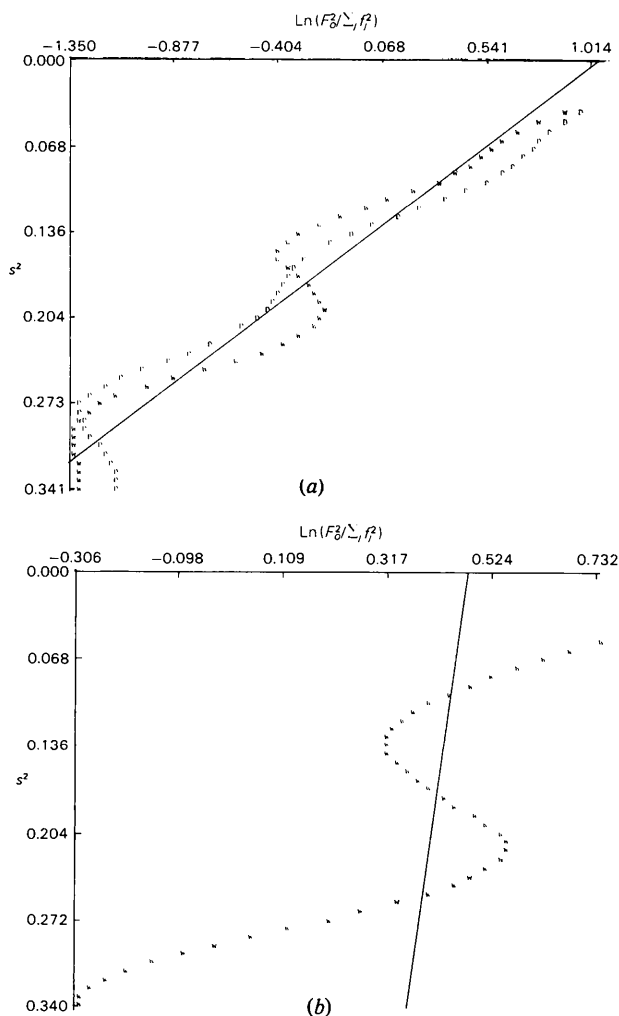


Fig. 1. (a) Wilson and Debye (obtained by introducing the known geometry of the phthalimido group) plots for LAKAT using both measured and generated reflexions, (b) Wilson plot with measured reflexions only.

Table 1. LAKAT: summary of the results of inserting the unobserved reflexions after dividing the reciprocal lattice into six shells of increasing $s = \sin \theta/\lambda$

$z = F^2/\langle F^2 \rangle$ indicates the normalized intensity and $\sigma(F)$ is the computed standard deviation of the inserted unobserved reflexions.

Shell no.	$s_{\text{lim}} (\text{\AA}^{-1})$	F_{min}	$\sigma(F)$	z_{min}	No. of observed reflexions	No. of generated reflexions	Total	% generated
1	0.1	20.9	3.0	0.044	8	1	9	11.1
2	0.2	10.3	1.5	0.009	51	4	55	7.3
3	0.3	12.1	1.8	0.069	115	21	136	15.4
4	0.4	12.7	1.8	0.309	125	118	243	48.6
5	0.5	12.6	1.8	0.553	116	268	384	69.8
6	0.6	13.1	1.9	1.824	16	465	481	96.7
Total					431	877	1308	67.0

$P2_12_12_1$ with $a = 11.940$, $b = 15.725$, $c = 7.018$ Å (Sikirica, Vicković & Viterbo, 1978a).

Only 431 independent reflexions were measured out of a total of 1308 within the limiting radius $s = 0.6$ Å⁻¹. The reflexions were divided into six shells and the unobserved ones were inserted as described above; the results are summarized in Table 1.

The data obtained in this way were then used as input to the *MULTAN* system (Declercq, Hull, Germain, Lessinger, Main & Woolfson, 1976).

The results are compared with those obtained using the measured reflexions only. In Fig. 1 the two Wilson (1942) plots show a great, but not unexpected improvement. However, the most relevant result is the easy solution of the structure, which came out entirely using the most consistent set of phases generated by *MULTAN*; no interpretable *E* map was obtained when the normalized amplitudes had been calculated using the measured reflexions only.

In a similar way we were able to solve the structure of 2-phthalimido-4-methylthio- γ -butyrolactone (Sikirica, Vicković & Viterbo, 1978b), crystallizing in the space group $P\bar{1}$ with four independent molecules (76 non-hydrogen atoms) in the asymmetric unit. Only 1828 reflexions were measured, constituting 37% of those within a sphere of radius $s = 0.66$ Å⁻¹. The solution was not as straightforward as for

LAKAT; only 57 out of 76 atoms were recognisable in the *E* map computed with the best set of phases. The completion and refinement of the structure showed that the observed data were not only poor in quantity but also in quality, as the crystal decomposed during the measurement.

In conclusion we wish to stress that the procedure described is a simple and rapid way to achieve the solution of reasonably complex structures by direct methods for the case where there is a large proportion of unobserved reflexions.

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The chemical and magnetic transformation of the series $\text{Ni}_x\text{Fe}_2\text{O}_4$. By K. N. SUBRAMANYAM and M. KADRI, Physics Department, Al Fateh University, Box 656, Tripoli, Libya

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Abstract

The gradual degradation of the cubic spinel phase in ferrimagnetic compounds of composition $\text{Ni}_x\text{Fe}_2\text{O}_4$ ($x = 1.0$ to 0.1) has been doubly confirmed by the X-ray diffraction and microwave initial magnetic-susceptibility measurements on the samples. The sharp ferrimagnetic–antiferromagnetic transition occurring at a composition corresponding to ($x = 0.1$) indicates a change in crystal symmetry.

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Introduction

The chemical and magnetic structures are well known for compounds like NiFe_2O_4 (ferrimagnet) and $\alpha\text{-Fe}_2\text{O}_3$ (canted antiferromagnet). However, information regarding the chemical and magnetic transformation of the series $\text{Ni}_x\text{Fe}_2\text{O}_4$ is not available in the published literature. In the present work, polycrystalline samples having compositions $\text{Ni}_x\text{Fe}_2\text{O}_4$ ($x = 1.0$ to 0.1) were prepared by sintering the

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