Fig. 1. Molecular dimensions of dibenzothiophene sulfone. The molecular orientation displayed is that of the [001] projection.

largest estimated error in bond length is 0·02 Å and the average error is 0·017 Å.

The molecular packing is quite reasonable with no intermolecular distances shorter than the sum of the normally accepted van der Waals radii.

The sulfur–carbon bond distance reported herein as 1·74 Å is in good agreement with those found in β-isoprene sulfone (Jeffrey, 1951) and cis-2-butene episulfone (Desiderato & Sass, 1967). The sulfur–oxygen bond distance of 1·49 Å is in good agreement with the value predicted from the sum of the Pauling double-bond covalent radii but is about 0·05 Å longer than that observed in other sulfones (Desiderato & Sass, 1967). In the remainder of the structure, the bond distances and angles are comparable to the equivalent values found for fluorene (Burns & Iball, 1955). The ring closing C(6)–C(6') distance of 1·46 Å is, within experimental error, equal to the value of 1·48 Å observed

for fluorene. The molecule, within experimental error, possesses C_{2v} symmetry.

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The cation distribution in CoFe₂O₄. By G. D. RIECK and J. J. M. THIJSSEN, Laboratory of Physical Chemistry, Technological University, Eindhoven, The Netherlands

The metal ions in $CoFe_2O_4$ when fired in air, are probably randomly distributed over the cation sites of the spinel structure.

As a part of a programme on the determination of the distribution of the cations in spinel type structures (Rieck & Driessens, 1966), we studied the structure of $CoFe_2O_4$ with respect to the occupation of the octahedral and tetrahedral sites by Co and Fe ions. If λ is the fraction of the tetrahedral sites occupied by Fe ions, the formula may be written $Co_{1-\lambda}Fe_\lambda[Co_\lambda Fe_{2-\lambda}]O_4$, the brackets indicating the ions in octahedral sites.

The spinel structures contain as unknown crystallographic parameter the coordinate (u) of the oxygen ions. The value of u may differ somewhat from its value in an

ideal spinel, viz. $\frac{3}{8}$, and both λ and u may change in relation to temperature and oxygen pressure during preparation.

The samples were made from $\alpha\text{-}Fe_2O_3$ (Merck, p.a.) and Co_3O_4 (Merck, p.a.), mixed according to the stoichiometric composition of $CoFe_2O_4$, pressed to tablets, fired for 24 hours in air at 1100°C, then powdered, pressed again and fired for 48–53 hours in air at 1200–1400°C. After this they were either quenched or slowly cooled in air and their cell constants a were measured (Table 1). In order to find λ we used the method of Bertaut (1950). We applied Co $K\alpha$ radiation in order to obtain a (maximum) difference between

Table 1. *Parameters of* CoFe₂O₄ *samples*

Sample No.	Firing temperature	Cooling in air	a	u	λ
1	1350°C	Quenched	8·387 Å	0·375	0·65
2	1200	Quenched	8·385	0·375	0·67
3	1350	Slowly cooled	8·393	0·375	0·63
4	1400	Quenched	8·386	0·376	0·68
5	1400	Slowly cooled	8·394	0·376	0·64

f_{Co} and f_{Fe}. We used the atomic scattering factors of Co^{2+} and Fe^{3+} as given in *International Tables for X-ray Crystallography* (1962) together with Cooper's (1963) dispersion corrections for Co K radiation. Both cations may (partly) have another valency, but using Co radiation in the case of sin θ/λ for reflexions such as 400, the differences between $f_{Co^{2+}}$ and $f_{Co^{3+}}$ as well as between $f_{Fe^{2+}}$ and $f_{Fe^{3+}}$ are negligible. The value of $f_{O^{2-}}$ has been taken from Tokonami (1965).

The parameters u and λ were graphically determined from a series of integrated reflexion intensities, measured on a Philips PW1310–1350 diffractometer with discriminator, at a velocity of $\frac{1}{8}°$ in 2θ per minute. The background intensity to be subtracted from the integral intensities has been measured by step-scanning during 200 sec for each $0·05°$ in 2θ, on both sides of each diffraction peak. We used the 111, 220, 400 and 440 reflexions on the grounds that they are (i) separated from other peaks, (ii) of sufficient intensity, (iii) sensitive to changes in u and λ. However, even under these circumstances the accuracy of λ does not exceed $\pm 10\%$.

The resulting u and λ values for different samples are given in Table 1.

We may conclude from the average value of λ of about $\frac{2}{3}$, that if CoFe₂O₄ has been prepared by firing in air, the distribution of the Co and Fe ions over the tetrahedral and octahedral sites is completely random. Neither of the ions has (under these circumstances) a preference for either of the sites and the formula can be written $Co_{1/3}Fe_{2/3}[Co_{1/3}Fe_{2/3}]_2O_4$.

We have found that firing in nitrogen or in oxygen changed the intensities of some of the reflexions appreciably. These differences may be due to a change in λ, to vacancies, or to ordering of the cations.

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Cell dimensions of some salts of malic acid. By H. SCHMITTLER, *Deutsche Akademie der Wissenschaften zu Berlin, Institut für Strukturforschung, Berlin-Adlershof, Germany,* (DDR)

The lattice constants and possible space groups of three malates have been determined by the X-ray powder method (Guinier type camera). The crystals of one malate are monoclinic and those of the other two are triclinic. The indexing was done by use of a computer program.

The four malates

(I) K(C₄H₅O₅).H₂O
(II) K₂(C₄H₄O₅).H₂O
(III) Fe(C₄H₅O₅)₂.4H₂O
(IV) Fe(C₄H₄O₅).2½H₂O

prepared by Anastasiadis & Ringpfeil (1966) have been investigated by X-ray powder method. The photographs were taken with Cu $K\alpha_1$ or Fe $K\alpha_1$ radiation in a Guinier-type camera. As₂O₃ (Swanson & Tatge, 1953) was used as a standard substance.

The powder patterns of three of the salts mentioned could be indexed and the cell dimensions (Table 1) were determined. The indexing and computational work was done with computer programs (Schmittler & Denner, 1965) for

the Zeiss computer ZRA 1. The main part of these is a zone-finding program similar to that described by de Wolff (1963). The Bravais lattice type for each of the malates (I), (II), and (III) has been derived from the character of their reduced cell and the Niggli matrix representation (Azaroff & Buerger, 1958). The possible space groups for salt I were concluded from systematic absences. In the triclinic cases the reduced cells are given.

The reliability of the determination is characterized by the quantity M introduced by de Wolff (1966):

$$M = Q_{max}/N \cdot \Delta .$$

Q_{max} means the largest value of $Q = 1/d^2$, N is the number of observed and indexed lines with $Q < Q_{max}$, and Δ is the average discrepancy between measured and calculated