Table 1. *Parameters of* $CoFe_2O_4$ *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 $\sin\theta/\lambda$ 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 ±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 $CoFe_2O_4$ 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.

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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) $K(C_4H_5O_5).H_2O$
(II) $K_2(C_4H_4O_5).H_2O$
(III) $Fe(C_4H_5O_5)_2.4H_2O$
(IV) $Fe(C_4H_4O_5).2\frac{1}{2}H_2O$

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. As_2O_3 (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):

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

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

Table 1. *Crystallographic data of some salts of malic acid*

	$K(C_4H_5O_5) . H_2O$	$K_2(C_4H_4O_5) . H_2O$	$Fe(C_4H_5O_5)_2 . 4H_2O$
a (Å)	8.608 ± 0.004	7.339 ± 0.003	7.468 ± 0.003
b	13.049 ± 0.004	8.549 ± 0.003	7.673 ± 0.003
c	7.249 ± 0.003	7.026 ± 0.002	7.376 ± 0.003
α (°)	90	102.83 ± 0.03	99.10 ± 0.02
β	118.60 ± 0.03	109.54 ± 0.03	103.67 ± 0.02
γ	90	92.60 ± 0.03	63.54 ± 0.02
Reliability index, M	39	29	34
Possible space groups	$C2/c$ or Cc	$P\bar{1}$ or $P1$	$P\bar{1}$ or $P1$
Number of formula units, Z	4	2	1
ϱ_{cal} (g.cm^{-3})	1.77	1.78	1.89
ϱ_{exp}	1.77	1.77	1.86

values of Q. $M > 10$ means complete reliability. The values of M given in Table 1 were calculated before minimizing the discrepancies with the aid of a computer program. After this procedure the quantities M increased by a factor of about four.

For the malates (I), (II), and (III) the lattice constants and possible space groups given in Table 1 result. The experimental density and the calculated value with Z formula units within the cell are given for each of the three malates. The powder pattern of salt (IV) could not be indexed. We suppose that the crystals are unstable in air and that the sample contained a mixture of some compounds when we received it.

No further work on these substances is contemplated.

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Re-examination of the crystal structure of ferroelectric tetragonal bronze-type $Ba_6Ti_2Nb_8O_{30}$. By P. B. JAMIESON and S. C. ABRAHAMS, *Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey, U.S.A.*

Stephenson's visually estimated $Ba_6Ti_2Nb_8O_{30}$ room temperature structure factors have been corrected for absorption, and for anomalous dispersion as is appropriate for measurements on a polar crystal. Least-squares refinement of his original model, with the corrected data, results in physically reasonable temperature factors and in more meaningful estimates of error in the atomic positions, as compared with the previously published values. The random distribution of the Nb and Ti atoms over the 10 available sites was confirmed. In the closely related structure of $Ba_{0.27}Sr_{0.75}Nb_2O_{5.8}$ the polar space group $P4bm$ transforms to the antipolar space group $P\bar{4}b2$ at higher temperature. The homopolar Nb/Ti composite atom in $Ba_6Ti_2Nb_8O_{30}$ is calculated, by analogy, to be displaced by 0.18 ± 0.10 Å for a similar transformation.

In the course of studying a series of ferroelectric tungsten bronze-type crystal structures, such as $Ba_{0.27}Sr_{0.75}Nb_2O_{5.8}$ (Jamieson, Abrahams & Bernstein, 1968), we became interested in the details of the study by Stephenson (1965) on the related material $Ba_6Ti_2Nb_8O_{30}$. Accurately determined atomic positions for this ferroelectric crystal would provide a valuable datum point in our recently discovered relationship between atomic displacements and both Curie temperature and spontaneous polarization (Abrahams, Kurtz & Jamieson, 1968). In the original work on tetragonal $Ba_6Ti_2Nb_8O_{30}$ ($a = 12.54 \pm 0.05$, $c = 4.01 \pm 0.01$ Å, space group $P4bm$) by Stephenson, neither absorption corrections nor allowance for the imaginary part of the atomic scattering factor dispersion were made. Neglect of these corrections in this polar crystal could introduce serious error into the resulting atomic coordinates.

Structure factors were calculated on the basis of Stephenson's final coordinates, using the scattering factors he quoted. The agreement between Stephenson's F_{obs} and F_{calc} values, as listed in his Table 2, corresponds to $R = 0.217$. Our F_{calc} values differed considerably [by a maximum of 67 electrons for $F(140)$] from his, and corresponded to $R = 0.196$. Our values were confirmed by an independent method of calculation. His coordinates were thereupon refined by the method of least squares, using Busing, Martin & Levy's (1962) *ORFLS* program. Each structure factor was assigned a weight given by $w(F_{obs}) = 1/(\sigma F_{obs})^2$, where

$$\sigma F_{obs} = 0.15 |F_{obs}| \text{ for } |F_{obs}| \geq 5 |F_{min}|,$$
$$\sigma F_{obs} = 0.75 |F_{min}| \text{ for } 4 |F_{min}| \leq |F_{obs}| < 5 |F_{min}|,$$

and