corresponding S functions and used as prescribed in Table 4.

A suggested procedure for calculating structure factors and derivatives is illustrated in Fig. 1. For each atom i, the trigonometric triple products $(T_{1-8})_i$ are first calculated. The intermediate products $(P_{1-32})_i$ are then formed, and these are combined to give the coefficients $(S_{1-8})_i$. (For an isotropic atom, only P_{1-8} need be calculated since $P_{1-8}=S_{1-8}$). Space group and index parity tests are then made, and if necessary the additional functions $(V_{1-8})_i$ or $(W_{1-8})_i$ are calculated. The correct structure factor and derivative terms are then selected in accordance with Table 4.

We have used these orthorhombic expressions and also the monoclinic expressions of RD as the bases for two separate structure factor and least-squares programs for the Burroughs 220 computer. This computer has an access time of approximately 100 microseconds; a complete structure factor least-squares calculation, including the collecting of 7 × 7 matrices involving scale and temperature-factor derivatives for each atom, takes approximately 0·25 seconds per atom reflection. Isotropic atoms, for which many of the calculations can be by-passed, require less than half this time.

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Least Squares Refinement of the Structure of Gadolinium-Iron Garnet, $Gd_3Fe_2Fe_3O_{12}$

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X-ray diffraction photographs of gadolinium–iron garnet, $Gd_3Fe_2Fe_3O_{12}$, show Laue symmetry *m*3*m*, and systematic extinctions indicate *Ia*3*d* as the most probable space group. There are eight formula weights per unit cell with $a = 12{\cdot}470 \pm 0{\cdot}005$ Å. Positions of all ions except O^{2-} are fixed by the space group. The least-squares method has been applied to refine the oxygen coordinates, using only 75 structure factors with significant oxygen contributions. The final values obtained for the coordinates are $x = -0{\cdot}0269$, $y = 0{\cdot}0550$, and $z = 0{\cdot}1478$. Interionic distances and angles calculated from these coordinates are nearly identical to the corresponding distances and angles in yttrium–iron garnet, as predicted by magnetic data.

Difficulties were encountered in the least-squares refinement of the structure. The use of limited numbers of structure factor data gave rise to large interactions between the temperature factors of the metal ions. A separate refinement with additional data was necessary to evaluate these thermal parameters.

Introduction

Gadolinium–iron garnet is one of a series of ferrimagnetic oxides of general formula $R_3Fe_2Fe_3O_{12}$, where R represents yttrium or a rare-earth element with $Z = 62$ to 71 inclusive. Bertaut & Forrat (1956) and Geller & Gilleo (1957*a*) have shown that these synthetic garnets have the same crystal structure as that of the natural garnets, which was established by Menzer (1928) from X-ray powder photographs. Similar compounds with aluminium or gallium replacing iron have also been prepared (Yoder & Keith, 1951; Keith & Roy, 1954). The first detailed X-ray single crystal work on the synthetic garnets has been carried out by Geller & Gilleo (1957*b*, 1959), who have refined the structure of yttrium–iron garnet. Because detailed information is of importance in understanding magnetic properties, it appears desirable to carry out structure analyses for other garnets to determine the effects of cation substitution upon the crystal structure.

The unknown parameters in the garnet structure are the oxygen–ion coordinates, the oxygen–ion temperature factor, and the temperature factors of the metal ions. The three oxygen coordinates are most significant. An accurate determination of these in the presence of the heavier metal ions must be based only on those reflections to which oxygen ions contribute significantly; therefore, only limited numbers of structure factor data are available for the analysis.

The object of the present work is an accurate measurement of the oxygen coordinates in gadolinium–iron garnet. The least-squares method of analysis should be most appropriate for refinement of the structure using a limited number of reflections; however, a difficulty arises in applying the method. The choice of reflection data to give highest accuracy in the oxygen coordinates introduces an artificial interdependence between the metal–ion temperature factors (see 'Discussion of the least-squares refinement'). The result may be complete failure of the least-squares program, or a calculation of erroneous values of the parameters. Means of avoiding this difficulty will be discussed.

Experimental

Single crystals of gadolinium–iron garnet were grown from a lead oxide flux, following the procedure of Nielsen & Dearborn (1958). A spherical sample of radius 0·0154 cm. was ground from one of these crystals, and was used to obtain the lattice constant measurements and intensity data. The crystal was oriented on a back-reflection Laue camera to a [110] direction, and then transferred to a Weissenberg camera for final adjustment.

A zero-level photograph was taken, and *hk*0 reflections from a quartz single crystal were superimposed on the same film as a calibration to accurately determine the lattice constants. Intensity data were collected, using the Weissenberg equi-inclination technique with Co $K\alpha$ radiation. The zero-layer line and all odd-numbered layer lines were recorded on multiple film packs consisting of four sheets of Ilford Industrial Type G film. Sixty-eight of 75 possible independent reflections on the odd-numbered layers were recorded; the remainder were too weak to be observed. Intensities of the observed reflections were judged visually and corrected for the Lorentz-polarization and velocity factors, using a portion of the Incor I program written by A. Zalkin and R. E. Jones* of the University of California Radiation Laboratory for the IBM 650 computer. Further corrections for the effects of absorption were obtained from the tables of Bond (1959). A common relative scale for the intensity data was then derived from 44 reflections which appear in equivalent forms on more than one layer line. Finally, the intensity data were converted to structure factors listed in Table 1 under F_o.

Crystallographic data

Single crystal photographs of gadolinium–iron garnet show Laue symmetry *m*3*m*, and establish the following conditions for non-extinction: (hkl), $h+k+l=2n$; $(hk0)$, $h=2n$, $k=2n$; (hhl), $l=2n$, $2h+l=4n$. The most probable space group, therefore, is $Ia3d(O_h^{10})$. Eight formula weights in the unit cell with $a=12{\cdot}470 \pm 0{\cdot}005$ Å give an X-ray density of 6·452 g.cm.$^{-3}$; the linear ab-

Table 1. *Observed and calculated structure factors for gadolinium–iron garnet*

hkl	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_c	F_c
121*	187	−206	7,10,1	102	117	893	15	−11
161	228	297	891	50	−52	9,10,3	44	−66
231	190	−163	8,11,1	13	−11	255	221	−219
251	274	−268	9,10,1*	71	−94	275	102	92
271*	154	−148	233	< 29	7	295*	127	−117
291*	117	−114	253	239	−222	2,11,5*	106	106
2,11,1	141	−139	273	96	77	475	68	65
2,13,1	56	−61	293*	125	−129	495	15	−15
341	105	103	2,11,3*	107	98	4,11,5	13	−10
361	119	−109	2,13,3	86	−102	565	157	172
381	< 29	−13	363	129	−118	5,10,5*	100	−96
3,10,1*	109	105	3,10,3*	143	127	675	167	163
451	24	−24	453	< 28	−19	695*	110	115
471	49	46	473	44	46	6,11,5*	79	97
491	61	−67	493	41	−39	785	< 18	6
4,11,1	31	−23	4,11,3	23	22	7,10,5	71	80
4,13,1	7	6	563	103	96	895	24	24
561*	152	155	583	73	−84	277	139	141
581	53	−55	5,10,3*	118	−115	297	92	−82
5,10,1	146	−153	5,12,3	32	37	2,11,7	99	110
5,12,1	< 22	−9	673*	116	−118	497	< 18	0
671	69	67	693*	111	−111	4,11,7	35	46
691	131	129	6,11,3	134	−150	677	72	−56
6,11,1*	90	91	783	< 21	−12	697	109	117
781	27	−29	7,10,3*	95	94	299	114	−126

* Oxygen contribution less than 10% of total structure factor.

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sorption coefficient for Co $K\alpha$ radiation ($\lambda = 1\cdot7902$ Å), based on this value of D_x, is 648·9 cm.$^{-1}$.

Least-squares refinement of the structure

The metal ions all occupy special positions in the unit cell of gadolinium–iron garnet; Fe^{3+} ions occupy positions 16(*a*) and 24(*d*), while Gd^{3+} ions are in positions 24(*c*) of *Ia*3*d*. Oxygen ions, however, are located in general positions 96(*h*) with three unknown coordinates.

A refinement of the oxygen coordinates by the least-squares method requires a selection of the structure factors to include only those with significant contributions, percentagewise, from the oxygen ions. Geller & Gilleo (1957) have shown that the class of reflections with two odd indices and one even index meets this requirement. Those with the even index divisible by four have contributions from the oxygen ions only. The remaining reflections with one even index receive no contribution from the Fe^{3+} ions in 16(*a*), and the scattering of the Gd^{3+} ions in 24(*c*) is always opposite in phase to the scattering from the Fe^{3+} ions in 24(*d*). Therefore, the least-squares refinements of the oxygen parameters in this work were based only on the aforementioned class of reflections; all those reflections having large over-all contributions from the metal ions were omitted from the least-squares analyses except in one instance when the thermal parameters of the metal ions only were refined.

The first attempt to refine the oxygen coordinates was set up to include only those reflections having contributions from the oxygen ions alone. Twenty-seven such reflections were used, of which twenty-one were observed. A comparison of these with the corresponding structure factors for yttrium–iron garnet (Geller & Gilleo, 1957; Geller & Gilleo, 1959) indicated that the oxygen parameters of the two structures were probably not greatly different. The oxygen parameters for yttrium–iron garnet were therefore used as the starting values in this refinement. The atomic scattering factors for the oxygen ions were based on tables published by Freeman (1959). These data were modified for doubly ionized oxygen so that $f_{O^{2-}} = 10\cdot00$ at $\sin\theta/\lambda = 0$ and $f_{O^{2-}} = f_O$ for $\sin^2\theta/\lambda^2 \geq 0\cdot05$. Calculations were carried out on the IBM 704 computer using the least-squares program of Busing & Levy (1959). All observed reflections were weighted 1·00; unobserved reflections were included and given weight 0·01. The least-squares solution converged very quickly, and parameter shifts became negligible after the second cycle of refinement. Table 2 shows the results of the first two and the final (fifth) cycle. Standard deviations computed for the final parameters are:

$$\sigma(x) = 0\cdot0009$$
$$\sigma(y) = 0\cdot0007$$
$$\sigma(z) = 0\cdot0007$$
$$\sigma(B_O) = 0\cdot42\ \text{Å}^2$$
$$\sigma(K) = 0\cdot028$$

The discrepancy factor, $R(=\Sigma||F_o|-|F_c||/\Sigma|F_o|)$, based on data from the final cycle, is 0·098 for all reflections; if unobserved reflections are excluded, the value is 0·093.

Table 2. *Least-squares refinement based on reflections produced by oxygen ions only*

Oxygen parameters	*x*	*y*	*z*	*B* (Å²)	*K*
Initial	−0·0274	0·0572	0·1492	2·05	1·085
Cycle 1	−0·0273	0·0544	0·1475	1·36	1·001
Cycle 2	−0·0274	0·0547	0·1477	1·32	0·999
Cycle 5	−0·0274	0·0547	0·1477	1·32	1·000

The next step in the structure refinement was to include the additional structure factors having contributions from both oxygen and metal ions. Proper weighting of these data required knowledge of the approximate size of the oxygen contribution to each reflection. This information was obtained from structure factor calculations based on the oxygen parameters obtained in the previous refinement. These calculations also showed that large dispersion corrections to the metal–ion scattering factors were necessary.* The real parts of the dispersion corrections for Gd^{3+} and Fe^{3+} were estimated, using procedures outlined by James (1953), and then adjusted to give the best agreement between observed and calculated structure factors for those reflections with small oxygen contributions (Table 1).† Corrections of thirteen electrons and three electrons for Gd^{3+} and Fe^{3+} respectively were obtained in this way. The Busing & Levy program was again used with the expanded list of reflections. The starting parameters for the oxygen ions were those from the final cycle of the previous refinement (Table 2); the initial thermal parameters for the metal ions were estimated as $B_{Fe} = 0\cdot63$ Å² and $B_{Gd} = 0\cdot50$ Å². All observed reflections were given a weight of 1·00 except those with an oxygen contribution less than 10% of the over-all structure factor; these were given weight 0·10. Unobserved reflections were included and given weight 0·01. This time, however, the refinement did not proceed satisfactorily; after one cycle, extremely large shifts were indicated for the metal–ion temperature factors ($\Delta B_{Gd} = 6\cdot07$, $\Delta B_{Fe} = 16\cdot67$). These shifts were obviously incorrect, and resulted in an increase of the discrepancy factor from 0·122 to 0·387.

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* The atomic scattering factors for Gd^{3+} and Fe^{3+} were taken from the tables of Thomas & Umeda (1957).

† The imaginary portions of the dispersion corrections were not included in the scattering factors. Calculations indicate that these corrections would have only a small effect on a few high-angle reflections with relatively large oxygen contributions. It appears unlikely, therefore, that inclusion of the imaginary portions would produce any significant changes in the oxygen coordinates, although slight changes in the temperature factors might be effected.

After several unsuccessful attempts to refine the data, we went to the Sayre NYXR2 least-squares program. Starting parameters and weights were the same as those used previously. At first, it appeared that the refinement was proceeding correctly. Reasonable values of the oxygen parameters ($x=-0\cdot0286$, $y=0\cdot0534$, $z=0\cdot1471$, $B_{\text{O}}=1\cdot58$) were computed. However, rather suspicious results were obtained for the metal–ion thermal parameters. These two parameters converged very slowly, and after ten cycles the program produced values of 0·59 Å^2 for Gd^{3+} and 0·18 Å^2 for Fe^{3+}. It seemed unlikely that the temperature factor of the heavier Gd^{3+} ion could be so much larger than that of the Fe^{3+} ion.

Finally, we returned to the Busing & Levy program and studied the progress of the least-squares refinement in some detail. It was then realized, as we will show in the next section, that the choice of reflections to determine most accurately the oxygen coordinates also precluded determination of the metal–ion thermal parameters.

In order to determine temperature factors for $\text{Gd}^{3+}(24c)$ and $\text{Fe}^{3+}(24d)$ it was necessary to include additional intensity data, consisting of reflections with three even indices. A number of these reflections were taken from a zero-level intensity record. Altogether, 14 independent reflections were observed, but several of these showed serious extinction effects. Eight of these structure amplitudes which appeared free of extinction were then grouped with a like number of structure factors having two odd indices and one even index, arbitrarily chosen from those listed in Table 1. These reflections were then used with the Busing & Levy program to refine the metal–ion thermal parameters only.* The calculations ran successfully and values of $B_{\text{Gd}}=0\cdot25$ Å^2 and $B_{\text{Fe}}=0\cdot49$ Å^2 were obtained; the observed and calculated structure factors from this refinement are given in Table 3.

The temperature factors obtained for Gd^{3+} and Fe^{3+} should be considered only as rather rough approximations, largely because of the limited numbers of data used. However, even with a larger number of reflections included in the refinement, the errors in estimating dispersion corrections would probably prevent an accurate determination of the thermal parameters.

Table 3. *Observed and calculated structure factors for refinement of metal–ion temperature factors*

hkl	F_o	F_c	*hkl*	F_o	F_c
224	564	566	3,10,1	109	105
251	274	−261	693	111	−113
440	246	−267	668	136	−144
561	152	157	695	110	119
660	140	−153	0,0,12	320	281
228	96	−81	2,2,12	359	370
291	117	−111	6,11,1	90	91
448	78	−72	7,10,3	95	92

The final refinement, again using the Busing & Levy program, was based only on the structure factors listed in Table 1. Seven parameters are involved in calculating these amplitudes; however, only the oxygen positional parameters were allowed to vary. The metal–ion temperature factors were held constant throughout the iterations because they are indeterminate from the structure factors used. The oxygen–ion thermal parameter and the scale factor were also held constant because of their sensitivity to errors in the metal–ion dispersion corrections.† The results of this refinement are given in Table 4 which lists the initial and final parameters. Table 1 gives a comparison of F_o versus F_c. Standard deviations of the oxygen coordinates, computed from the final parameters, are:

$$\sigma(x)=0\cdot0007$$
$$\sigma(y)=0\cdot0005$$
$$\sigma(z)=0\cdot0005$$

The discrepancy factor for all reflections is 0·084; if unobserved reflections are excluded, the same value is obtained.

Discussion of the least-squares refinement

The difficulty encountered in refining a limited number of structure factors is only one example of a more general problem deriving from interactions which may occur between parameters in the course of solving the normal equations of least-squares. Geller (1960) has made a comprehensive study of this general problem of parameter interaction; for this reason, the present

Table 4. *Final least-quares refinement of gadolinium–iron garnet*

	Oxygen coordinates						
Parameters	*x*	*y*	*z*	B_{O} (Å^2)*	B_{Gd} (Å^2)*	B_{Fe} (Å^2)*	*K**
Initial	−0·0274	0·0547	0·1477	1·32	0·25	0·49	1·000
Cycle 1	−0·0270	0·0550	0·1478	—	—	—	—
Cycle 2	−0·0270	0·0550	0·1478	—	—	—	—
Cycle 3	−0·0269	0·0550	0·1478	1·32	0·25	0·49	1·000

* Parameter held constant throughout refinement.

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* Only the temperature factors of the $\text{Gd}^{3+}(24c)$ ions and the $\text{Fe}^{3+}(24d)$ ions were allowed to vary; the temperature factor of the $\text{Fe}^{3+}(16a)$ ions was assigned an arbitrary value of 0·50 Å^2 and held constant during the refinement.

† The work of Geller & Gilleo (1957*b*, 1959) on yttrium–iron garnet has demonstrated the strong interaction between the oxygen-ion thermal parameter and the metal–ion dispersion corrections.

discussion will be limited to the specific case of the garnet structure.

The problem in this case is best understood by studying the steps involved in a complete solution of the least-squares matrix, such as that employed by the Busing & Levy program. Parameter shifts are calculated from the relationship

$$\Delta p_i = \sum_j b_{ij} v_j\,, \tag{1}$$

where b_{ij} is the inverse matrix element and v_j is the vector of the normal equations. The inverse element is in turn obtained from

$$b_{ij} = \tilde{a}_{ji}/|a_{ij}|\,, \tag{2}$$

where $\tilde{a}_{ji}$ represents the adjoint matrix and $|a_{ij}|$ the determinant of the direct matrix. Now if the derivative cross-terms involved in this determinant should always have the same sign, then their summations become quite large, and it is seen that the magnitude of the determinant approaches zero. The size of the inverse matrix element, and hence the magnitude of the parameter shift, are controlled by small differences between very large quantities in the denominator of (2). In such a case the calculated shifts will be meaningless unless extremely accurate structure factor measurements are available.

The situation described above applies to the problem encountered in determining the thermal parameters of gadolinium–iron garnet. Contributions to the overall structure factors from Gd^{3+} and Fe^{3+} are always opposite in sign for the class of reflections with h, k odd and $l=2n$ (h, k, l permutable). As a result, the cross terms involving the temperature factors of the two metal ions always have the same sign, and the determinant approaches the point of vanishing.

The best solution to this problem appears to be one of choosing a group of structure factors in which the phase relationships between the metal–ion contributions vary; in this way, the large cross-term summations are avoided. This method was used to obtain the metal–ion temperature factors used in the final refinement of gadolinium–iron garnet.

A possible alternative is to use a least-squares program such as NYXR2 in which the off-diagonal terms are omitted from the solution. This, of course, avoids the computational difficulty arising from large cross terms. However, it is doubtful whether the results will have any significance with respect to those parameters involved in the cross terms. This is most clearly seen in the erroneous temperature factors obtained in the refinement with NYXR2. It is also seen in the small differences between the oxygen coordinates calculated in this same run and those obtained in the final refinement with the Busing & Levy program (Table 4). A study of the matrix elements showed relatively large cross-term interactions among the oxygen positional coordinates, although their size does not approach that of the interactions between the metal–ion thermal parameters.*

It was further seen that interactions between thermal parameters and the oxygen coordinates are quite small. This is very fortunate as it indicates that the lack of accurate temperature factors does not seriously affect the determination of the oxygen positions.

Discussion of the structure

The interionic distances and the more important interionic angles in gadolinium–iron garnet, based on the final set of oxygen coordinates (Table 4), are given in Table 5. The standard deviations of the metal–oxygen and oxygen–oxygen interionic distances are ±0·008 Å and ±0·015 Å respectively; for interionic angles the standard deviation is ±0·4°.

A comparison of the data in Table 5 with the corresponding interionic distances and angles for yttrium–

Table 5. *Interionic distances and angles in gadolinium–iron garnet*

$Fe^{3+}(a)$ octahedron	$Fe^{3+}(a)$–O^{2-}	(6) 2·00 Å*
	O^{2-}–O^{2-}	(6) 2·67, (6) 2·97
$Fe^{3+}(d)$ tetrahedron	$Fe^{3+}(d)$–O^{2-}	(4) 1·89
	O^{2-}–O^{2-}	(2) 2·89, (4) 3·19
$Gd^{3+}(c)$ dodecahedron	$Gd^{3+}(c)$–O^{2-}	(4) 2·38, (4) 2·47
	O^{2-}–O^{2-}	(4) 2·67, (4) 2·87
		(2) 2·89, (2) 3·02
	$Fe^{3+}(a)$–$Fe^{3+}(d)$	(6) 3·49
	$Fe^{3+}(a)$–$Gd^{3+}(c)$	(6) 3·49
	$Fe^{3+}(d)$–$Gd^{3+}(c)$	(2) 3·12, (4) 3·82
	$Fe^{3+}(a)$–O^{2-}–$Fe^{3+}(d)$	127·4°
	$Fe^{3+}(a)$–O^{2-}–$Gd^{3+}(c)$	105·1° (2·38), 102·1° (2·47)†
	$Fe^{3+}(d)$–O^{2-}–$Gd^{3+}(c)$	92·8° (2·38), 121·4° (2·47)
	$Gd^{3+}(c)$–O^{2-}–$Gd^{3+}(c)$	103·7°

* Numbers in parentheses preceding interionic distances refer to the relative numbers of such distances.

† Numbers in parentheses following bond angles refer to Gd^{3+}–O^{2-} interionic distances.

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* The neglect of cross-terms is actually not the *ultimate* reason for discrepancies between the diagonal approximation and complete solution. More exactly, the neglect of cross-terms results in an apparent, but not true, convergence of the diagonal approximation (see Geller, 1960).

iron garnet (Geller & Gilleo, 1957*b*) shows that the two structures are quite similar in detail. The differences in distances and angles can be accounted for by the increase in size of the Gd^{3+} ion over that of Y^{3+}. It is particularly interesting to note that the interionic angle $Fe^{3+}(a)$–O^{2-}–$Fe^{3+}(d)$ is 127·4° in gadolinium–iron garnet, compared to 126·6° in yttrium–iron garnet. The difference between these two angles is practically insignificant. This finding appears to support the conclusions reached by Pauthenet (1958) from his study of the paramagnetism and Curie temperatures of rare-earth–iron garnets, including gadolinium–iron garnet. He has found that the Curie temperatures of all of these garnets are very similar and close to that of yttrium–iron garnet. Because the paramagnetic behavior of the rare-earth ions indicates only weak interactions on them, the Curie points must be determined by interactions between Fe^{3+} ions, which are the same for the different iron garnets.

Possibly, the most significant differences between gadolinium–iron garnet and yttrium–iron garnet are in the O^{2-}–O^{2-} interionic distances in the oxygen dodecahedron about Gd^{3+}. These distances are such as to make the dodecahedron slightly more irregular in gadolinium–iron–garnet than in yttrium–iron garnet.

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An Attempt to Determine the Structure Parameters of Condensed Ring Hydrocarbons Using the Electron-Diffraction Method in Gas Molecules

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Electron diffraction studies have been carried out to determine the molecular structure of naphthalene, anthracene, and coronene, using least-squares refinement. For naphthalene a set of structure parameters are obtained of approximately the same accuracy as those from the X-ray crystallographic studies (Table 2). For anthracene the present study leads to ambiguity, and no single set of parameters can be presented (Table 4). For coronene the investigation leads to a unique set of values for the C–C bond distances, but the standard deviations are so large that at least two of the distance values must be considered as rather uncertain (Table 6).

Introduction

The ambitions of molecular structure chemists as to the accuracy of bond-distance determination seem to continue to increase. In particular the problem of accurate bond-distance determination of aromatic molecules is continually attracting the interest of both theoreticians and experimentalists. The simple one-ring aromatic molecules, benzene, pyridine, and furan, have been studied using Raman spectroscopy (Stoicheff, 1954; Stoicheff & Langseth, 1956), microwave spectroscopy (Bak, Hansen-Nygaard & Rastrup-Andersen, 1958), and electron diffraction (Almenningen, Bastiansen & Hansen, 1955; Almenningen, Bastiansen & Fernholt, 1958), and the bond distances have been determined with an accuracy of 0·001–