the thermodynamically stable room-temperature phase,[10] for its having a lower density than that of the α phase, and allows us to make a speculation regarding the structure of the recently discovered ferrimagnetic (and piezoelectric) Ga$_{2-x}$Fe$_x$O$_3$.[3]

DETERMINATION OF THE STRUCTURE

The crystals used in this study were prepared by J. P. Remeika.[3] Powdered specimens gave photographs in agreement with the patterns reported by Kohn et al.[4] and by Foster and Stumpf[10] for the β-Ga$_2$O$_3$. Most of the crystals photographed were twinned, some multiply, but after some searching one was found from which a small single-crystal segment with long direction along the monoclinic b axis was cleaved. The cell constants[11] $a = 12.23 \pm 0.02$, $b = 3.04 \pm 0.01$, $c = 5.80 \pm 0.01$ A, $\beta = 103.7 \pm 0.3°$ given by Kohn et al.[4] are quite accurate for our purposes as established by the complete indexing of the powder pattern taken with CuKα radiation (see Appendix). The space group to which the crystal belongs was reported by Kohn et al. to be C_{2h}^3, which is indeed the most probable one and with which all our data are compatible. There are 4 Ga$_2$O$_3$ in the unit cell;[4] the x-ray density is therefore 5.94 g/cm.

The crystal photographed with the Weissenberg camera and both CuKα and MoKα radiation had the dimensions: length 1.3 mm and cross section 0.09$\times$0.11 mm. The diffraction symmetry was C_{2h}-$2/m$, with systematic absences, hkl, $h+k \neq 2n$. Thus the possible space groups are C_{2h}^3-$C2/m$, C_s^3-Cm and C_2^3-$C2$. The space group Cm would require two equivalent atoms related by the symmetry plane to be at a maximum distance from each other of 1.52 A thus indicating that the crystal cannot possibly belong to this space group.

The corresponding intensities on the even-numbered (Weissenberg) layers about the b axis were very similar as were those on the odd-numbered layers. Thus the structure appeared to be layered at one-half the b axis. It was therefore unlikely that the heavy atoms would be at combinations of positions such that the y coordinates differed by other than multiples of $\frac{1}{2}b$, (although, of course very small deviations might occur). In such a case the positions of $C2$ with $y=0$ or $\frac{1}{2}$ become special positions of $C2/m$. Negative tests for piezo- and pyroelectricity supported the conclusion that the most probable space group for the crystal is $C2/m$.

In $C2/m$, the general positions and positions e-h would require two equivalent atoms related by the symmetry plane to be at 1.52 A from each other. Thus atoms could not be in any of these positions.

The intensities were estimated visually by comparison with a calibrated intensity scale and by cross comparison of intensities on various photographs. Intensities of zero-level data taken with MoKα radiation were averaged with those taken with CuKα radiation when observable with both radiations. (The small dispersion corrections for Ga would not have a significant effect.) Because no really new information was obtainable from other than the zero and first layers, intensities on these were the only ones quantitatively estimated.

Because absorption of both radiations by the crystal was high ($\mu_{CuK\alpha} = 299$ cm^{-1}, $\mu_{MoK\alpha} = 255$ cm^{-1}), it was necessary to use a small crystal (see above). Thus maximum exposure times for the photographs taken with MoKα radiations were 102, 90, 70, and 90 hr for the zero through third layers, respectively. With CuKα radiation, the maximum exposure times were about 20 hr. Absorption corrections were applied assuming the crystal to be cylindrical with an average radius of 0.05 mm. The absorption correction tables used were those of Bond[12] and applied to the first layer in accordance with the formula given by Bond.[12] (see also footnote reference 13). Lorentz-polarization-Tunell rotation-factor corrections were also applied.[14]

A Patterson projection on (010) clearly showed the peaks resulting from Ga—Ga interactions, and it appeared that all atoms must lie in the symmetry planes, and occupy five sets of positions $4i$: (000, $\frac{1}{2}\frac{1}{2}0) \pm (x0z)$. It was also clear that the contributions from the Ga^{3+} ions would determine most of the phases. It was necessary to consider the first-layer data for the purpose of distinguishing the most probable among homomorphic (010) projections. A (010) Fourier synthesis, a generalized Patterson projection using the $h1l$ data, a generalized Fourier projection with the $h1l$ data, and a pseudo-three-dimensional difference synthesis aided in determining the oxygen-ion positions. The pseudo-three-dimensional synthesis was done as follows: The contributions of the Ga^{3+} ions were subtracted from the observed structure factors. These had been scaled on the basis that, as indicated, the contributions of oxygens were generally not large. Thus some intuition entered into this scaling and as will be seen appeared to be quite sound. The remainders assumed to be the oxygen contributions, but of course containing numerous error contributions, were used in the synthesis. Each such amplitude, $h0l$, and $h1l$ was counted once in the synthesis. As expected, some spurious peaks occurred. Nevertheless, having obtained fairly accurate positions of the Ga^{3+} ions, the results of this synthesis together with structural considerations led to a determination of the oxygen trial parameters.

The trial parameters (for refinement) are given in Table I. It should be mentioned that the oxygen-ion positions were expected to be quite inaccurate, the idea being to save the author time by allowing the IBM 704 computer to do all of the refining.

[10] L. M. Foster and H. C. Stumpf, J. Am. Chem. Soc. 73, 1590 (1951).

[11] Our designation of the axes is in keeping with the convention $c < a$ for the monoclinic cell.

[12] W. L. Bond, Acta Cryst. 12, 375 (1960).

[13] M. J. Buerger and N. Niizeki, Am. Mineral. 43, 726 (1958).

[14] I am indebted to Dr. R. G. Treuting for programing the calculation of the corrected relative squared structure amplitudes and relative structure amplitudes on the IBM 704 computer.