The MSS method calculates the scale factor $G_{p,r}$ for the pth of the n batches at iteration r and the scaled structure factors $F^2_{h,r}$ for reflection h at iteration r from:

$$F^2_{h,r}=\sum_p (G_{p,r-1}F^2_{hp}w_{hp})/\sum_p (G^2_{p,r-1}w_{hp}) \tag{1}$$

$$G_{p,r}=\sum_h (F^2_{h,r}F^2_{hp}w_{hp})/\sum_h [(F^2_{h,r})^2w_{hp}]\,, \tag{2}$$

where w_{hp} is the weight given to the observational equation for reflexion h in batch p. Usually $w_{hp}=1/\sigma^2_{hp}$ and σ_{hp} is the standard deviation of reflection h in batch p.

The iterations terminate when $|(F^2_{h,r}-F^2_{h,r-1})/F^2_{h,r-1}|\le\varepsilon$ for all h, and MSS use $\varepsilon=0{\cdot}003$. It can be seen from Table 1 that we require many iterations to get stable values of G_p. This is because MSS yields changes in $G_{p,r}$ which are as small as 1/30 of the errors in $G_{p,r}$. Error estimates based on the shifts can therefore underestimate the errors by this factor. This behaviour can be explained by formulating the MSS equation to give shifts in $G_{p,r}$. The MSS equations then have the same right-hand sides as the HRS equations but the matrix of the HRS equations is replaced by a diagonal matrix with larger elements.

We have used a method in which equation (2) is replaced by

$$A_p=\sum_h \{w_{hp}(F^2_{h,r})^2+w^2_{hp}F^2_{hp}(F^2_{hp}-2F^2_{h,r}G_{p,r-1})/(\sum_j w_{hj}G^2_{j,r-1})\} \tag{3}$$

$$G_{p,r}=G_{p,r-1}+\sum_h (w_{hp}F^2_{h,r}F^2_{hp})/A_p - G_{p,r-1}\sum_h [(w_{hp}(F^2_{h,r})^2]/A_p\,. \tag{4}$$

This is a correct diagonal approximation to the HRS equations. It can be unstable because the shifts can be too large. We have dealt with this in the method called FR in Table 1 by limiting the shifts, normalizing to make $G_{1,r}=1$ for all r and then applying a simple acceleration device. The procedure is to replace equation (4) by

$$C_{p,r}=G_{p,r-1}+\sum_h (w_{hp}F^2_{h,r}F^2_{hp})/A_p-G_{p,r-1}\sum_h [w_{hp}(F^2_{h,r})^2]/A_p \tag{5}$$

$$D_{p,r}=\max(C_{p,r},\ 0{\cdot}5\ G_{p,r-1}) \tag{6}$$

$$E_{p,r}=D_{p,r}/D_{1,r} \tag{7}$$

$$\mathbf{i}_r\quad=\mathbf{E}_r-\mathbf{G}_{r-1},\ \text{where } \mathbf{G}_r=(G_{1,r},\ \ldots,\ G_{n,r})\ etc. \tag{8}$$

$$\mathbf{G}_r\quad=\mathbf{G}_{r-1}+\mathbf{a}_r\ \text{where} \tag{9}$$

$$\mathbf{a}_r\quad=\mathbf{i}_r/(1-K)\ \text{and} \tag{10}$$

$$K\quad=\mathbf{a}_{r-1}\,.\,\mathbf{i}_r/\mathbf{a}_{r-1}\,.\,\mathbf{a}_{r-1}\,. \tag{11}$$

K is set equal to 0 in cycle 1 and is limited so that $K\le 0{\cdot}3$ to avoid excessive extrapolation. Note that similar acceleration of the MSS process would have little effect unless dangerously large values of $1/(1-K)$ were used.

We conclude that the FR method is likely to be the quickest if the number of scale factors is greater than 4 and the whole of the calculation can be performed in a rapid-access store. If, on the other hand, the data must be fetched from a slow peripheral device such as magnetic tape then the FH method has fewest cycles and the original HRS method should only be used if an efficient latent roots and vectors routine is not available. The MSS method is relatively slow and does not provide a reliable estimate of the computing error.

References

Fox, G. C. & Holmes, K. C. (1966). *Acta Cryst.* **20**, 886.

Hamilton, W. C., Rollett, J. S. & Sparks, R. A. (1965). *Acta Cryst.* **18**, 129.

Monahan, J. E., Schiffer, M. & Schiffer, J. P. (1967). *Acta Cryst.* **22**, 322.

Acta Cryst. (1968). B**24**, 294

Misuse of the 'riding' model in correcting bond lengths for effects of thermal motion*.

By George M. Brown, *Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A.*

(*Received* 9 *October* 1967)

Some examples are cited of misuse of the 'riding' model of Busing and Levy. The appropriateness of the model for a particular bond should be assessed by consideration of the physical situation. Meaningful use of the model can lead only to positive bond-length corrections.

In recent reports of crystal-structure analyses several authors have incorrectly used the 'riding' model of Busing & Levy (1964) as embodied in the computer program *ORFFE* of Busing, Martin & Levy (1962), with the result that 'corrections' to bond lengths for the effects of thermal motion have been reported which are totally devoid of meaning. Instances of misuse of the riding model have been noted in oral presentations, in manuscripts prepared for publication, and, surprisingly, in at least six published papers. The occurrence of such errors may result in part from the fact that the program *ORFFE* was widely distributed before the appearance of the paper (Busing & Levy, 1964) which presented the theory of the riding-model correction.

One misconception evidenced in the published papers (Enrione, Boer & Lipscomb, 1964; Boer, Streib & Lipscomb, 1964; Hall, Perloff, Mauer & Block, 1965; Boer, 1966; Voet & Lipscomb, 1967; Friedman & Lipscomb, 1966) is the notion that the mean interatomic separation $\bar{S}$ as calculated by Busing & Levy can be less than the separation S_0 of the mean positions of the two atoms or, in other words, that corrections for thermal motion can be negative. Busing & Levy (1964) show that $\bar{S}$ is never less than S_0. The program *ORFFE*, however, will allow the unwary user to compute a value of $\bar{S}$ less than S_0. The

---

* Research sponsored by the U.S. Atomic Energy Commission under contract with Union Carbide Corporation.

equation by which the program computes $\bar{S}$ for the case of atom B riding on atom A is

$$\bar{S} = S_0 + (w_B^2 - w_A^2)/2S_0 \,,$$

where w_A^2 and w_B^2 are the mean-square displacements of atoms A and B perpendicular to the bond A–B. A calculated value $\bar{S}$ less than S_0 shows that $w_B^2 - w_A^2$ is negative, as it was never intended to be, and that the assumption that B rides A is completely unjustified. If the assumption is justified according to the definition given by Busing & Levy for the riding model, $w_B^2 - w_A^2$ will necessarily be positive or zero, and the calculated $\bar{S}$ will be greater than or equal to S_0.

Of course, a positive correction computed with the program does not in itself imply that use of the riding model is justified. Justification can only be based on an analysis of the physical situation which establishes that the model is a good approximation for the particular bond in question. In this connection some further remarks are necessary concerning the misuse of the riding model in the papers cited above. Most of the bonds for which meaningless 'corrections' have been calculated are bonds within the framework structures of cage-like or basket-like borane or carborane compounds. It is obvious that the riding model is inappropriate for such bonds; they clearly do not satisfy the defining condition for applicability of the riding model that 'the vector separation be independent of the position of one of the atoms, A, . . .' or the condition that . . . 'if atom B is much lighter than atom A and is strongly linked only to A, the lighter atom may be thought to 'ride' on the heavier one in the manner described'. The proper way to obtain meaningful corrections for such bonds is to perform a rigid-body analysis by the method of Cruickshank (1956) or by the more general method of Schomaker & Trueblood (1968) and subsequently to apply corrections for molecular libration by the procedure outlined by Busing & Levy (1964). The simple riding model is also not applicable in general to the correction of the lengths of bonds in rings or chains.

References

Boer, F. P. (1966). *J. Amer. Chem. Soc.* **88**, 1572.

Boer, F. P., Streib, W. E. & Lipscomb, W. N. (1964). *Inorg. Chem.* **3**, 1666.

Busing, W. R. & Levy, H. A. (1964). *Acta Cryst.* **17**, 142.

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFFE, A Fortran Crystallographic Function and Error Program.* Oak Ridge National Laboratory, Tennessee, Report TM-306.

Cruickshank, D. W. J. (1956). *Acta Cryst.* **9**, 754.

Enrione, R. E., Boer, F. P. & Lipscomb, W. N. (1964). *Inorg. Chem.* **3**, 1659.

Friedman, L. B. & Lipscomb, W. N. (1966). *Inorg. Chem.* **5**, 1752.

Hall, L. H., Perloff, A., Mauer, F. A. & Block, S. (1965). *J. Chem. Phys.* **43**, 3911.

Schomaker, V. & Trueblood, K. N. (1968). *Acta Cryst.* In the press.

Voet, D. & Lipscomb, W. N. (1967). *Inorg. Chem.* **6**, 113.

Acta Cryst. (1968). B**24**, 295

Crystallographic study of cerium aluminate ($CeAlO_3$)*.

By Y. S. Kim, *Bell Telephone Laboratories, Inc., Allentown, Pennsylvania, U.S.A.*

(*Received* 25 *September* 1967)

Cerium aluminate, $CeAlO_3$, has been successfully prepared in chemically homogeneous form. The rhombohedral lattice constants, $a = 5{\cdot}327$ Å and $\alpha = 60°15'$, fall on smooth curves with those for the isostructural aluminates of La, Pr, and Nd (space group $R\bar{3}m$) investigated by Geller & Bala [*Acta Cryst.* (1956). **9**, 1019].

Cerium aluminate, a double trioxide compound, *i.e.*, $A^{3+}B^{3+}O_3$, is known to be one of the perovskite types. However, the synthesis of the compound in chemically homogeneous form has been unsuccessful by the usual methods because of the chemical instability of cerium trioxide. The crystal structure of $CeAlO_3$ has been determined by other investigators (Roth, 1957; Schneider, Roth & Waring, 1961); it is rhombohedral, space group $R\bar{3}m$, and similar to that of certain other rare earth aluminates, $REAlO_3$, investigated by Geller & Bala (1956). In the work of the former authors a second phase CeO was found to be present when $CeAlO_3$ was prepared in helium atmosphere. In the present note further refined structural data are reported for homogeneous $CeAlO_3$ which was successfully synthesized *in vacuo*.

In preparing $CeAlO_3$ the stable cerous oxalate, $Ce(C_2O_4)_3.xH_2O$, was used as the source of Ce^{3+}, and C.P. grade alumina was used. An intimately mixed powder, proportioned to contain a 1:1 mole ratio of Ce_2O_3 and Al_2O_3, was heated to 1600°C for one hour in a vacuum furnace (10^{-6} torr). Both microscopic and X-ray diffraction analysis of the reacted material revealed that it was single phase Ce_2O_3.

Lattice constants of the $CeAlO_3$ were determined from high-angle lines in the Debye–Scherrer patterns obtained with Cr $K\alpha$ radiation at room temperature.

In Table 1 good agreement can be seen between the observed and the calculated values of interplanar spacings. The very weak lines ($h+k+l=$ odd) were, however, extremely difficult to detect in the powder patterns. The lattice constants of $CeAlO_3$ are tabulated below:

Rhombohedral primitive cell	Triply primitive hexagonal cell	Pseudocell dimension
$a = 5{\cdot}327 \pm 4$ Å	$a = 5{\cdot}348 \pm 4$ Å	$a = 3{\cdot}774 \pm 4$ Å
$\alpha = 60°\,15' \pm 2'$	$c = 13{\cdot}021 \pm 5$ Å	$\alpha = 90°\,13' \pm 3'$.

The edge length of the perovskite-like 'pseudocell' (which corresponds to omission of the weak $h+k+l=$ odd reflections) is half that of the quadruple primitive face-centered

---

* Part of the M.S. degree thesis at N.C. State College (1958).