Acta Cryst. (1974). A30, 234

An X-ray Study of Thermal Vibrations in Sodium

BY D. W. FIELD AND E. H. MEDLIN

Department of Physics, University of Adelaide, Adelaide, South Australia

(*Received* 5 *June* 1973; *accepted* 20 *September* 1973)

A room-temperature X-ray study of Bragg reflexions from sodium metal crystals has been made. Six sets of integrated relative intensities were recorded photographically from two single crystals. Considerable anisotropy in the intensities has been found and it is suggested that this is due to anharmonic vibrations of the atoms. The data has been analysed in terms of a fourth-order atomic-potential expansion and values of an isotropic Debye parameter and an anharmonic anisotropic vibration parameter are given. The observed values of the available structure factors are presented. The accuracy claimed is 2%.

Introduction

Recent X-ray and neutron diffraction investigations of metal crystals have yielded a range of information about the crystals. The characteristic electronic structure of the alkali metals of an inert gas core and a single valence electron makes them the most fundamental of metals in theoretical physics, but their resulting chemical nature is somewhat intractable and there are few diffraction studies of the alkali metals to be found in the literature. An X-ray diffraction investigation has been undertaken for sodium single crystals to provide for the first time accurate X-ray data on scattering amplitudes and vibration properties of that metal. The alkali metals are body-centred-cubic at room temperature with space group $Im3m$. The value of the lattice parameters used in this work was $a_0=4{\cdot}2906$ Å (*American Institute of Physics Handbook*, 1963).

Sodium is the most convenient of the alkali metals to consider for single-crystal X-ray studies in terms of the usual criteria of crystal size and absorption properties. It is also convenient in that more experimental evidence relevant to the present study is available than for other alkali metals. For example, Fermi-surface measurements (Grimes & Kip, 1963; Shoenberg & Stiles, 1964), positron annihilation experiments (Donaghy & Stewart 1967) outer-electron momentum-density distribution experiments (Phillips & Weiss, 1968) and many other pieces of physical information indicate that sodium has the most nearly-free-electron-like character of all the alkali metals. On the other hand, sodium elastically is an highly anisotropic solid and it has a relatively low melting point and Debye temperature. Since these depend on the atomic vibration properties of the metal, it might be expected that the vibration would be large and anisotropic.

Experimental

The crystals used in the work were grown by the following technique. A few cm^3 of freshly cut sodium of $3N$ purity were placed under paraffin oil and melted. Samples of length about 1 cm were sucked into a standard capillary tube of bore $\sim 0{\cdot}5$ mm and wall thickness 0·01 mm. The tubes were cut to appropriate lengths and the ends sealed in a flame. The samples were then drawn axially at a more or less optimum rate of 2·2 cm per hour from an open bath of paraffin oil held at a constant temperature (± 1 °K) a few degrees higher than the melting point of sodium (~ 371 °K). There was no preferred orientation of the crystals. The rotation axes chosen were identified by means of stereographic projections of transmission Laue films, then accurately by the method of Davies (1950).

Six sets of integrated relative intensity measurements were recorded from two separate sodium crystals. The intensities were recorded on four-film packs with an integrating Weissenberg camera and filtered radiation. The film densities were measured by microdensitometry. Some experimental details of the data sets, which are numbered in the order that they were measured, are given in Table 1.

Table 1. *Details of the data sets*

Data set	Crystal	Radiation	Crystal rotation axis
1	1	Cu $K\alpha$	$\langle 001\rangle$
2	1	Mo $K\alpha$	$\langle 001\rangle$
3	2	Cu $K\alpha$	$\langle 001\rangle$
4	2	Cu $K\alpha$	$\langle 210\rangle$
5	2	Mo $K\alpha$	$\langle 210\rangle$
6	2	Mo $K\alpha$	$\langle 001\rangle$

Substantial extinction was present in all samples. To reduce the effect of extinction, crystal 2 was immersed in liquid air immediately before intensity set 3 was recorded, and the sets of measurements at two different wavelengths were recorded for each crystal to allow a wavelength-dependent investigation of the extinction. However, sets 3 and 4, and similarly sets 5 and 6, were not scaled together because it was found that sodium undergoes a slow annealing process at room temperature after being treated with liquid air. That is, for crystals allowed to stand at room temperature after immersion in liquid air, intensities of the low-angle reflexions continued to decrease over several days and even weeks.

All the intensity sets were corrected for spot shape, Lorentz–polarization, absorption, anomalous dispersion and thermal diffuse scattering (TDS) effects. Lonsdale (1942) was first to point out the extremely complex TDS pattern for sodium, due largely to its elastically anisotropic nature. The only description of TDS-correction procedures considered suitable was that first-order procedure of Rouse & Cooper (1969), which takes into account elastic anisotropy. The scattering cross-section was derived from the elastic constants of Martinson (1969) and integrated over the volume swept out in reciprocal space as determined from the measured spot sizes using the idea of Annaka (1962) that the spot size can be used as a measure of the 'aperture' for film recording techniques. The first-order anisotropic TDS-correction factors so obtained were applied to each independent reflexion for each set.

Intensity data

The data sets were initially scaled by Wilson's (1942) method. Plots of $\ln[I(hkl)/F_c^2(hkl)]$ *versus* $\sin^2\theta/\lambda^2$ were drawn, where the values of the calculated structure factors $F_c(hkl)$ used were calculated from the free-atom wave function of Hartree & Hartree (1948), that is, in the absence of thermal motion. [We have been able to show that the difference in structure factors $F_c(hkl)$ used above and those calculated from a relativistic Hartree–Fock wave function by Doyle & Turner (1968) are $\sim 0{\cdot}1\%$, indicating that the relativistic effect in a light atom such as sodium is negligible for the present purpose.] The plot of $\ln[I(hkl)/F_c^2(hkl)]$ for data set 3 is shown in Fig. 1. The major features of the anisotropy in the higher-order intensities and the extinction in the lower-order intensities are clearly visible. The errors shown in the Figure were calculated from the spread in intensities of symmetry-related reflexions as the standard error of the mean intensity. Plots from the five sets showed similar features. Set 3, however, had the least calculated errors and the least anisotropy and extinction (see Table 2).

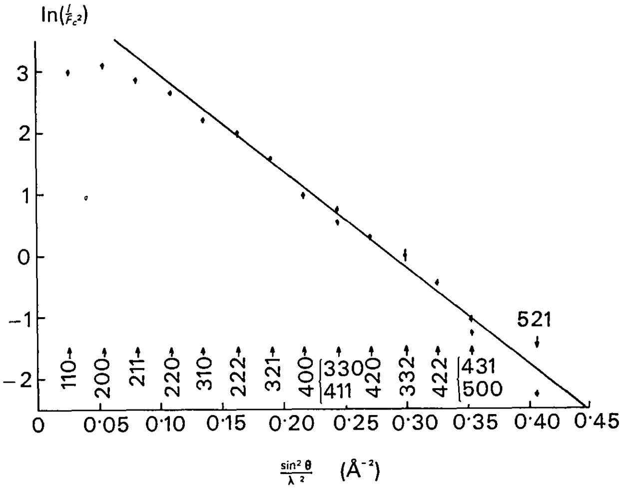

Fig. 1. Data plot for set 3. The straight line was fitted from reflexion 222 to reflexion 521. The vertical bars show estimated errors.

The causes of the anisotropy

Anisotropy such as that shown in Fig. 1 may be the result either of non-spherical atomic charge distributions or anharmonic atomic vibrations, or both. Using Dawson's (1967*a*) generalized structure-factor formalism to take account of both these effects, the structure factor for a b.c.c. monatomic solid such as sodium can be written as

$$F(\mathbf{S}) = \sum_j (\bar{f}+\delta f_4)\,(\bar{T}+\delta T_4)\cos 2\pi(\mathbf{S}\,.\,\mathbf{r}_j) \qquad (1)$$

where

$$|\mathbf{S}| = \frac{2\sin\theta}{\lambda},$$

$\bar{f}$ is the normal spherically symmetric scattering factor,

δf_4 is a fourth-order anisotropic correction term to $\bar{f}$,

$\bar{T}$ is the spherically symmetric temperature factor,

δT_4 is a fourth-order correction term to $\bar{T}$.

Here, $F(\mathbf{S})$, and hence the overall scattering and temperature factors are centrosymmetric because of the *m*3*m* point symmetry for all the (identical) atoms. Effects due to non-spherical charge distributions have been studied, for example, in diamond (Dawson, 1967*b*) and studies on fluorites (Dawson, Hurley & Maslen, 1967) have yielded information on the effects of anisotropic vibrations of atoms in solids. In the present study it was considered that the anisotropic effects observed were due to anisotropic vibrations of the atoms alone, that is $\delta f_4 = 0$ in equation (1). The measurement temperature of ~293 °K for the intensity sets was almost twice the Debye temperature of 152 °K obtained from heat-capacity measurements (*e.g.* Martin, 1965), indicating large atomic vibration amplitudes, and sodium elastically was known to be highly anisotropic. It has previously been mentioned that many pieces of physical evidence point to sodium having almost spherical valence-electron distribution, thus making it unlikely that any non-spherical electron-density features contributed to the results in Fig. 1.

Analysis of the anisotropy

The analysis was carried out on the basis of Willis's (1969) theory as follows. Willis showed that anharmonic vibrational effects in solids may be treated by assuming an Einstein model, and expanding the atomic potential to the power appropriate to the symmetry of the structure. In the case of a b.c.c. monatomic solid, the appropriate expansion is to fourth order given by

$$V(u_1,u_2,u_3)=V_0+\tfrac{1}{2}\alpha r^2+\gamma r^4-\delta(u_1^4+u_2^4+u_3^4-\tfrac{3}{5}r^4)$$

where u_1,u_2,u_3, are the components of the displacement **u** of the atom from its mean position, and $r^2=u_1^2+u_2^2+u_3^2$. The centrosymmetric temperature factor then becomes

$$\begin{aligned}T_c=N\exp\left[\frac{-Q^2k_BT}{2\alpha}\right]\Bigg\{&1-15k_BT\left[\frac{\gamma}{\alpha^2}\right]\\&+10(k_BT)^2\left(\frac{2\pi}{a_0}\right)^2\left[\frac{\gamma}{\alpha^3}\right](h^2+k^2+l^2)\\&-(k_BT)^3\left(\frac{2\pi}{a_0}\right)^4\left[\frac{\gamma}{\alpha^4}\right](h^2+k^2+l^2)^2\\&-(k_BT)^3\left(\frac{2\pi}{a_0}\right)^4\left[\frac{\delta}{\alpha^4}\right](h^4+k^4+l^4-\tfrac{3}{5}(h^2+k^2+l^2)^2)\Bigg\}\end{aligned}\tag{2}$$

where

$$N=\left\{1-15k_BT\left[\frac{\gamma}{\alpha^2}\right]\right\}^{-1},$$

$$Q=\frac{4\pi\sin\theta}{\lambda},$$

T is the absolute temperature and k_B is the Boltzmann constant.

For sodium this expression has been modified by letting

$$\begin{aligned}A=N\Bigg\{&1-15k_BT\left[\frac{\gamma}{\alpha^2}\right]+10(k_BT)^2\left(\frac{2\pi}{a_0}\right)^2\left[\frac{\gamma}{\alpha^3}\right]\\&\times(h^2+k^2+l^2)\\&-(k_BT)^3\left(\frac{2\pi}{a_0}\right)^4\left[\frac{\gamma}{\alpha^4}\right](h^2+k^2+l^2)^2\Bigg\},\end{aligned}$$

$$Y=N(k_BT)^4\left(\frac{2\pi}{a_0}\right)^4\left[\frac{\delta}{\alpha^4}\right],$$

$$P=Y/A\ ,$$

$$D(hkl)=h^4+k^4+l^4-\tfrac{3}{5}(h^2+k^2+l^2)^2$$

when the temperature factor then becomes

$$T_c=A\exp\left[\frac{-B\sin^2\theta}{\lambda^2}\right][1-PD(hkl)]\ .$$

If the isotropic anharmonic parameter γ is small, then $A\sim 1$, and it can be incorporated as a small change in the Debye parameter as

$$T_c=\exp\left[\frac{-B'\sin^2\theta}{\lambda^2}\right][1-PD(hkl)]\ .\tag{3}$$

The temperature factor T_c is now in the form

$$T_c=\bar{T}+\delta T_4\tag{4}$$

used in equation (1), but now the terms B' and $\bar{T}$ in equations (3) and (4) respectively are not harmonic, but contain some isotropic anharmonic terms.

The determination of the isotropic and anisotropic vibration parameters

The two parameters B' and P were determined by the following modification of Wilson's (1942) method for scaling intensities. Least-squares values of B' and K were determined by the solution of the equation

$$I(hkl)=KF_1^2(hkl)\exp\left[\frac{-2B'\sin^2\theta}{\lambda^2}\right]$$

for all non-extinction affected reflexions hkl, where

$$F_1(hkl)=F_c(hkl)\,[1-PD(hkl)]$$

and initially P was taken to be 0. Values of the 'observed' structure factors $F_o(hkl)$ in the absence of thermal motion were then calculated from the equation

$$I(hkl)=KF_o^2(hkl)\exp\left[\frac{-2B'\sin^2\theta}{\lambda^2}\right].$$

The value of P giving the best least-squares fit of the $F_1(hkl)$ to the $F_o(hkl)$ values was found. The procedure was then recycled to find new values for K, B' and P until convergence was reached. This occurred after two or three cycles for all data sets except set 6, where there were insufficient non-extinction-affected reflexions for the calculations to be performed. The values obtained for the least-squares parameters from each data set are listed in Table 2.

Table 2. *Isotropic and anisotropic vibration parameters*

Data set	B' (Å^2)	$P(\times 10^{-4})$
1	8·48	−9·83
2	8·95	−19·2
3	7·86	−7·01
4	7·54	−9·37
5	7·97	−11·2
6	8·50	−10·0

Mean $B'=8{\cdot}16\pm0{\cdot}25$ Å^2
Mean $P=-11{\cdot}3\pm2{\cdot}1\times10^{-4}$

The average value for B' and P given in each case is the value obtained from the first five sets. The values of $B'=8{\cdot}50$ Å^2 and $P=-10{\cdot}0\times10^{-4}$ given for set 6 were arbitrarily chosen and gave a good fit to the observed results.

Structure factors

The room-temperature values of the observed, calculated and corrected structure factors for intensity set 3 are given in Table 3 together with values for $\sin\theta/\lambda$ and the 'reliability' indices R and R_1. In the Table, the $F_{\rm obs}$, $F_{\rm calc}$, $F_{\rm corr}$ correspond to the absolute zero values F_o, F_c, F_1 each multiplied by $\exp(-B'\sin^2\theta/\lambda^2)$ using the appropriate B' for set 3. The indices R and R_1 were calculated as

$$R=\frac{\sum_{hkl}|F_o(hkl)-F_c(hkl)|}{\sum_{hkl}|F_o(hkl)|}$$

and

$$R_1=\frac{\sum_{hkl}|F_o(hkl)-F_1(hkl)|}{\sum_{hkl}|F_o(hkl)|}$$

where the summations were taken only over those reflexions *hkl* which were not affected by extinction. The mean error in $F_{\text{obs}}(hkl)$ calculated from the spread of intensities of symmetry-related reflexions is about 2·6%. This method of calculation probably gives an overestimate of the errors since for all data sets the mean calculated error is larger than the factor R_1. The claimed accuracy for the structure factors presented is 2%.

Table 3. *Observed, calculated and corrected room temperature structure factors*

Reflexions	$\frac{\sin\theta}{\lambda}$	F_{obs}	F_{calc}	F_{corr}
110	0·165	8·17	14·26	14·26
200	0·233	7·61	10·27	10·23
211	0·286	6·11	7·48	7·50
220	0·330	5·02	5·49	5·51
310	0·369	3·68	4·06	4·01
222	0·404	3·05	3·01	3·06
321	0·436	2·28	2·25	2·28
400	0·466	1·58	1·69	1·59
330	0·494	1·30	1·28	1·28
411	0·494	1·18	1·28	1·23
420	0·521	0·99	0·97	0·95
332	0·547	0·79	0·73	0·78
422	0·571	0·61	0·57	0·59
431	0·594	0·42	0·43	0·45
510	0·594	0·38	0·43	0·37
521	0·638	0·24	0·25	0·24

$R=0·049$
$R_1=0·019$

The Debye temperature

If the isotropic anharmonic effects are assumed to be small, (*i.e.* parameter γ is small in the fourth-order potential expansion), a value for the Debye temperature Θ_D can be derived with some physical sense from the isotropic Debye parameter B' by the usual formula for monatomic cubic crystals. The value of Θ_D obtained in this way from the mean value of $B'=8·16\pm0·25$ Å^2 (Table 2), is $\theta_D=134\pm2$ °K, corresponding to an r.m.s. vibration amplitude of $0·56\pm0·01$ Å. Values of Debye temperature determined by specific-heat methods of measurement have produced values of $\Theta_D\sim150$–160 °K (*e.g.* Martin, 1965; Lien & Phillips, 1960; Gammer & Heer, 1960; Roberts, 1957; Blackman, 1955). Other X-ray determinations of Θ_D for sodium by Dawton (1937), Geshko, Kushta & Mik'halchenko (1968), and Kumar, Valvoda & Viswamitra (1971), have yielded values for Θ_D of 120 ± 4 °K (estimated from a graph), 154 ± 8 and 140 ± 1 °K respectively. Since the present X-ray measurement of Θ_D is the only one to take account of each of TDS, extinction and anharmonic effects in sodium, it must be regarded as the most reliable.

The value of $\Theta_D\sim134$ °K obtained in the present study is about 14% lower than the average of available Debye temperatures obtained from specific-heat measurements on sodium. It is interesting that this is consistent with the experience of other authors, where for example, Wilson, Skelton & Katz (1966) found that the Debye temperatures based on elastic constants were about 17 and 10% greater than the X-ray values for nickel and chromium respectively. On the other hand, in the case of diamond, where the Debye temperature is much higher than that for either of the three previously mentioned elements, Schoenig & Vermuelen (1969) report a difference of only 2% between X-ray and heat-capacity measurements of Θ_D.

Anharmonic potential parameters

The expression for temperature factor T_c in equation (2) is not conveniently arranged for determination of values of the potential parameters since these vary with temperature. Following Willis (1969), a suitable form can be found by assuming that the potential parameters vary with temperature as

$$\frac{\alpha}{\alpha_0}=\frac{\gamma}{\gamma_0}=\frac{\delta}{\delta_0}=1-2\gamma_G\chi T$$

where $\alpha_0,\gamma_0,\delta_0$ are the potential parameters for no expansion, γ_G is the Gruneisen parameter, χ is the expansion coefficient, and it is assumed that $2\gamma_G\chi T\ll1$. For this work, values of $\gamma_G=1·25$ and $\chi=20·1\times10^{-5}$ °K^{-1} have been taken from Geshko *et al.* (1968).

The exponent of the Debye–Waller factor can then be written

$$\begin{aligned}2W= & \left(\frac{2\pi}{a_0}\right)^2(h^2+k^2+l^2)\left[\frac{1}{\alpha_0}\right]k_BT\\ & +\left(\frac{2\pi}{a_0}\right)^2(h^2+k^2+l^2)\left[\frac{2\gamma_G\chi}{\alpha_0k_B}\right](k_BT)^2\\ & -\left(\frac{2\pi}{a_0}\right)^2(h^2+k^2+l^2)\left[\frac{20\gamma_0}{\alpha_0^3}\right](k_BT)^2\\ & +\left(\frac{2\pi}{a_0}\right)^4(h^2+k^2+l^2)^2\left[\frac{2\gamma_0}{\alpha_0^4}\right](k_BT)^3\\ & -\left(\frac{2\pi}{a_0}\right)^4(h^2k^2+h^2l^2+k^2l^2-\tfrac{1}{3}(h^4+k^4+l^4))\\ & \times\left[\frac{12\delta_0}{5\alpha_0^4}\right](k_BT)^3.\end{aligned}\tag{5}$$

If relative integrated intensities have been measured at four or more temperatures for one or more reflexions, the values for the parameters $\alpha_0, \gamma_0, \delta_0$ may be determined explicitly. For a single-temperature measurement, the relation

$$\frac{\delta_0}{\alpha_0^4} = \frac{-P\left(\frac{a_0}{2\pi}\right)^4}{(k_BT)^3}$$

can be derived from a comparison of equations (3) and (5). The relation obtained in this way from the mean value of P (Table 2) is

$$\frac{\delta_0}{\alpha_0^4} = 15{\cdot}3 \text{ eV}^{-3} \text{ Å}^4$$

indicating the large contribution of the anisotropic anharmonic term δ_0 relative to α_0.

Conclusions and discussion

The present work represents the first vibrational anharmonicity analysis from X-ray Bragg diffraction data from a b.c.c. solid. Previous structures for which vibrational anisotropy has been studied have been adequately treated by the quasi-harmonic theory [*e.g.* KCl, (Willis, 1969)] or a third-order potential expansion [*e.g.* the fluorite structures, (Willis, 1969)]. The large highly anisotropic atomic vibrations in sodium crystals are, as might be expected, of greater amplitude toward the next-nearest neighbours in the ⟨100⟩ directions and of lesser amplitude toward the nearest neighbours in the ⟨111⟩ directions.

These results relate well with other physical information. For example, Glyde & Taylor (1972) have shown in a study of lattice dynamics in sodium that anharmonic effects are clearly important at room temperature, and Sangal & Sharma (1971) have shown that an anharmonic theory cannot account satisfactorily for the variation in Debye–Waller factor of sodium with temperature.

The group of alkali metals all have similar physical properties to sodium, with, for example, lower melting points and estimated Debye temperatures with increasing atomic number. It could be expected that all the alkali metals would be highly anharmonic and that all would have large and anisotropic vibration properties. (A study of potassium is proceeding in this laboratory).

This work was supported in part by the Australian Research Grants Committee. One of us (DWF) acknowledges the support of a Commonwealth Postgraduate Award.

References

American Institute of Physics Handbook (1963). 2nd ed. pp. 9–6.
Annaka, S. (1962). *J. Phys. Soc. Japan*, **17**, 846–853.
Blackman, M. (1955). *Handbuch der Physik*, Vol. VII, Pt. 1, p. 364. Edited by S. Flügge. Berlin: Springer Verlag.
Davies, P. T. (1950). *J. Sci. Instrum.* **27**, 338.
Dawson, B. (1967*a*). *Proc. Roy. Soc.* A**298**, 255–263.
Dawson, B. (1967*b*). *Proc. Roy. Soc.* A**298**, 264–288.
Dawson, B., Hurley, A. C. & Maslen, V. W. (1967). *Proc. Roy. Soc.* A**298**, 289–306.
Dawton, R. H. V. M. (1937). *Proc. Phys. Soc.* **49**, 294–306.
Donaghy, J. J. & Stewart, A. T. (1967). *Phys. Rev.* **164**, 396–398.
Doyle, P. A. & Turner, P. S. (1968). *Acta Cryst.* A**24**, 390–397.
Gammer, R. E. & Heer, C. V. (1960). *Phys. Rev.* **118**, 955–957.
Geshko, E. I., Kushta, G. P. & Mik'halchenko, V. P. (1968). *Ukr. Fiz. Zh.* **13**, 1788–1792.
Glyde, H. R. & Taylor, R. (1972). *Phys. Rev.* B**5**, 1206–1213.
Grimes, C. C. & Kip, A. F. (1963). *Phys. Rev.* **132**, 1991–1998.
Hartree, D. R. & Hartree, W. (1948). *Proc. Roy. Soc.* **193**, 299–304.
Kumar, S. K., Valvoda, V. & Viswamitra, M. A. (1971). *Curr. Sci.* **40**, 459–460.
Lien, W. H. & Phillips, N. E. (1960). *Phys. Rev.* **118**, 958.
Lonsdale, K. (1942). *Proc. Phys. Soc.* **54**, 314–353.
Martin, D. L. (1965). *Phys. Rev.* **139**A, 150–160.
Martinson, R. H. (1969). *Phys. Rev.* **178**, 902–913.
Phillips, W. C. & Weiss, R. J. (1968). *Phys. Rev.* **171**, 790–800.
Roberts, L. M. (1957). *Proc. Phys. Soc.* **70**B, 744–752.
Rouse, K. D. & Cooper, M. J. (1969). *Acta Cryst.* A**25**, 615–621.
Sangal, S. K. & Sharma, P. K. (1971). *Z. Phys. Chem. Liepz.* **247**, 257–264.
Schoenig, F. R. L. & Vermeulen, L. H. (1969). *Solid State Commun.* **7**, 15–18.
Shoenberg, D. & Stiles, P. J. (1964). *Proc. Roy. Soc.* A**281**, 62–91.
Willis, B. T. M. (1969). *Acta Cryst.* A**25**, 277–300.
Wilson, A. J. C. (1942). *Nature, Lond.* **250**, 152.
Wilson, R. H., Skelton, E. F. & Katz, J. L. (1966). *Acta Cryst.* **21**, 635–638.