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Neutron Diffraction Study of Anharmonic Thermal Vibration in $AuGa_2$

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Anharmonic effects are observed in a room-temperature neutron diffraction study of the intermetallic fluorite compound $AuGa_2$. The analysis is performed on the basis of a single anharmonic vibrational parameter in addition to the harmonic vibrational parameters. It yields the values $\alpha_{Au}=3{\cdot}08\ (0{\cdot}11)\times 10^{-12}$ erg Å^{-2}, $\alpha_{Ga}=2{\cdot}91\ (0{\cdot}08)\times 10^{-12}$ erg Å^{-2} for the harmonic parameters and $\beta_{Ga}=-2{\cdot}3\ (1{\cdot}2)\times 10^{-12}$ erg Å^{-3} for the cubic anharmonic parameter. The Debye temperature is determined to be $\Theta^M=169(3)$ K at 294 K. Neglect of the thermal diffuse scattering correction is found to introduce an error of $\sim 10\%$ in the Debye–Waller factors obtained. Least-squares analyses using the Zachariasen and the Becker & Coppens extinction corrections are found to give equivalent results.

Introduction

Recent diffraction studies of compounds with the fluorite structure have revealed significant anharmonic contributions to the thermal vibration. Ionic fluorites in which these effects have been observed include UO_2 (Willis, 1963), BaF_2 (Cooper, Rouse & Willis, 1968), CaF_2 (Cooper & Rouse, 1971; Strock & Batterman, 1972; Harvey & Prager, 1975) and SrF_2 (Cooper & Rouse, 1971; Mair & Barnea, 1971). Similar effects have also been observed in Mg_2Si (Cooper & Panke, 1970) and Mg_2Sn (Skelton, Lin & Rothberg, 1974), both of which have the anti-fluorite structure. The object of the present paper is to report a neutron diffraction determination of the temperature parameters of another fluorite structure, the intermetallic compound $AuGa_2$, in which similar anharmonic effects were observed.

Theory

A satisfactory account of diffraction effects due to anharmonicity in fluorite-type structures was first given by Dawson, Hurley & Maslen (1967) in terms of the generalized structure-factor formalism of Dawson (1967). Since Willis (1969) has recently presented a comprehensive review which treats these effects, we omit a detailed discussion of the theory here. Suffice it to say that the vibration of an atom j is assumed to be governed by an effective one-particle potential $V_j(\mathbf{u})$ which conforms to the site symmetry of the atom. To third-order terms in a power-series expansion, the potential function takes the form

$$V_j(\mathbf{u})=V_{0j}+\tfrac{1}{2}\alpha_j(u_1^2+u_2^2+u_3^2)+\beta_j(u_1u_2u_3) \qquad (1)$$

where the harmonic parameter α_j is related to the mean-square displacement u_j^2 and the usual Debye–Waller exponent B_j by

$$\alpha_j=kT/u_j^2=8\pi^2kT/B_j\,.$$

β is the cubic anharmonicity parameter, which is zero for the Au atoms (point symmetry $m3m$) and non-zero for the tetrahedrally coordinated Ga atoms (point symmetry $\bar{4}3m$).

The structure-factor expressions obtained within this approximation are:

$$\begin{aligned} F(hkl) &= 4b_{Au}T_{c,\,Au}+8b_{Ga}T_{c,\,Ga} && \text{for } h+k+l=4n\\ &\ 4b_{Au}T_{c,\,Au}-8b_{Ga}T_{c,\,Ga} && \text{for } h+k+l=4n+2\\ &\ 4b_{Au}T_{c,\,Au}\mp 8b_{Ga}T_{a,\,Ga} && \text{for } h+k+l=4n\pm 1 \end{aligned}$$

where

$$T_{c,j}=\exp\left[\frac{-8\pi^2kT}{\alpha_j}\sin^2\theta/\lambda^2\right]=\exp\left[-B_j\sin^2\theta/\lambda^2\right]$$

$$T_{a,\,Ga}=T_{c,\,Ga}(kT)^2\left(\frac{2\pi}{a}\right)^3\frac{\beta_{Ga}}{\alpha_{Ga}^3}\,hkl\,.$$

Experimental details

The sample was a large (0·3 cm)^3 single crystal of $AuGa_2$, kindly supplied by Dr C. M. Perrott of the Division of Tribophysics, C.S.I.R.O. It had been prepared from 99·999% pure material by induction heating within a double-walled quartz vessel and subsequent slow cooling in an electric furnace. The lattice constant obtained from a least-squares analysis of all the reflexions we measured was $a=6{\cdot}0754\ (20)$ Å at $T=294$ K, in good agreement with the value $a=6{\cdot}0758\ (10)$ Å at $T=296$ K obtained by Warren, Shaw, Menth, Di Salvo, Storm & Wernick (1973).

Integrated intensities of 137 reflexions, comprising 34 inedpendent reflexions, were measured in the ω–2θ mode using a four-circle diffractometer. The scan range was $\omega_0\pm\frac{1}{2}^\circ$ and stationary background measurements were made at $\omega_0\pm\frac{3}{2}^\circ$. The neutron wavelength was 0·981 Å and the measurement temperature 294 K.

Data analysis and results

Absorption was considerable, with $\mu(AuGa_2)=1{\cdot}01$ cm^{-1}, $\mu R\sim 0{\cdot}5$. Therefore the measured intensities were corrected for absorption by use of the program *DRACULA* (Elcombe, Cox, Pryor & Moore, 1971) which incorporates a five-point Gaussian integration scheme for the numerical evaluation of absorption factors and mean path lengths in a crystal of arbitrary shape.

Intensities were corrected for the first-order acoustic mode contribution to thermal diffuse scattering (TDS) with the program of Rouse & Cooper (1968). While this program was originally developed for X-rays, it can be applied with equal validity in the present case since the neutrons are faster than sound both for longitudinal and transverse acoustic modes (Willis, 1969). The program requires the use of a constant κ (Nilsson, 1957) which is a function of the elastic moduli. Schwartz (1964) has pointed out that Nilsson's (1957) general expression for κ includes implicit assumptions about the elastic moduli. His more general expression (which includes an artificial singularity – Walker & Chipman, 1969) was evaluated numerically by taking the Cauchy principal value of the singular integral. The value of κ so obtained for $AuGa_2$ was $10{\cdot}0\times10^{-10}$ N^{-1} m^{-2} with an anisotropy factor $2C_{44}/(C_{11}-C_{12})=2{\cdot}22$, compared to κ_{approx} (Nilsson)$=9{\cdot}82\times10^{-10}$ N^{-1} m^{-2}. These values fit very nicely on the graph of $\kappa/\kappa_{\text{approx}}$ *versus* anisotropy factor given by Walker & Chipman (1969). The simplified expression for κ given by these authors was also evaluated and found to be correct. The elastic moduli of $AuGa_2$ required for these calculations have been obtained by Testardi (1970); at 294 K the values are $C_{11}=10{\cdot}07\times10^{11}$, $C_{12}=7{\cdot}37\times10^{11}$, $C_{44}=3{\cdot}00\times10^{11}$ (dyn cm^{-2}).

Preliminary Wilson plots [$F^2(hkl)$ *versus* $\sin^2\theta/\lambda^2$] indicated substantial extinction in the stronger reflexions – those with $h+k+l=4n$ or $4n\pm1$. The plot for reflexions with $h+k+l=4n+2$ was reasonably linear (indicating low extinction) and provided an initial estimate of the harmonic temperature parameters: $\bar{B}=0{\cdot}95$ Å^2.

Least-squares analyses of the data were performed with two different programs. The first of these is a version of the standard crystallographic program *ORFLS* (Busing, Martin & Levy, 1963) which was modified by Fehlmann (1968) to include Zachariasen's (1967) extinction correction and re-modified by Mair (1971) to include the third-order anharmonic parameter β for anions in the fluorite structure. The second and more flexible program is a non-linear least-squares regression program using numerical differentiation. The structure-factor expressions may be written down explicitly in this program. It is therefore quite straightforward to include as many anharmonic terms as required for the analysis of any relatively simple structure, and to investigate variants of the extinction correction (Harvey & Prager, 1975). We used the recent extinction formalism of Becker & Coppens (1974*a*,*b*) and assumed a Lorentzian distribution of crystallites in the mosaic crystal.

The following parameters were allowed to vary in the least-squares refinements: scale factor s; the ratio b_{Au}/b_{Ga} of the scattering amplitudes of gold and gallium; the harmonic vibrational parameters α_{Au} and α_{Ga}; the anharmonic vibrational parameter β_{Ga}; and the effective domain radius r^* for the Zachariasen extinction correction, or the domain radius r and the mosaic distribution parameter g for the Becker & Coppens extinction correction. All reflexions (averaged over equivalents) were given unit weight in the refinements. The agreement index used is $R=\sum|\Delta F_{\text{meas}}|/\sum|F_{\text{meas}}|$.

The final values of parameters are shown in Table 1. Results of a refinement on the data before the TDS correction was applied is also included (column 2). Table 2 lists the structure factors, extinction factor $y^{1/2}$ and TDS correction t corresponding to the refinement in column 4 of Table 1. F_o represents the observed structure factors (reduced to unit scale) after correction for extinction and TDS, *i.e.*

$$F_o=F_{\text{obs}}/[s\,.\,y^{1/2}\,.\,(1+t)^{1/2}].$$

The following final values were obtained for the extinction parameters: $r^*=8{\cdot}5\times10^{-7}$ cm (Zachariasen) and $r=5\times10^{-5}$ cm, $g=1\times10^4$ (Becker & Coppens). The value we obtained for the ratio of scattering lengths $b_{Au}/b_{Ga}=1{\cdot}032$ (10) is significantly lower than the ratio (1·056) calculated from the literature values $b_{Au}=0{\cdot}76\times10^{-12}$ cm, $b_{Ga}=0{\cdot}72\times10^{-12}$ cm (Neutron Diffraction Commission, 1972).

Table 1. *Results of refinements*

	Zachariasen extinction before TDS correction	Zachariasen extinction after TDS correction	Becker & Coppens extinction after TDS correction
b_{Au}/b_{Ga}	1·033 (0·009)	1·033 (0·009)	1·032 (0·010)
α_{Au}(10^{-12} erg Å^{-2})	3·33 (0·10)	2·98 (0·08)	3·08 (0·11)
B_{Au}(Å^2)	0·96 (0·03)	1·08 (0·03)	1·04 (0·04)
α_{Ga}(10^{-12} erg Å^{-2})	3·10 (0·06)	2·83 (0·05)	2·91 (0·08)
B_{Ga}(Å^2)	1·03 (0·02)	1·13 (0·02)	1·10 (0·03)
$-\beta_{Ga}$(10^{-12} erg Å^{-3})	2·5 (1·3)	1·9 (1·0)	2·3 (1·2)
R	0·0107	0·0110	0·0106

Discussion

The harmonic vibrational parameters α_{Au} and α_{Ga} in $AuGa_2$ at room temperature are found to be equal within experimental error. The weighted mean value is $\alpha=2{\cdot}97$ (0·09)$\times10^{-12}$ erg Å^{-2}; this corresponds to a weighted mean value of $B=1{\cdot}08$ (0·03) Å^2 for the Debye–Waller factor and $[u^2]^{1/2}=0{\cdot}117$ (0·003) Å for the r.m.s. harmonic displacement.

From the relationship (see Skelton, Lin & Rothberg, 1974):

$$\tfrac{1}{3}(m_{Au}B_{Au}+2m_{Ga}b_{Ga})=\frac{6\pi^2}{k\Theta}\left[\frac{\Phi(\Theta/T)}{\Theta/T}+\frac{1}{4}\right]$$

(where m_{Au}, m_{Ga} are the atomic masses and $\Phi(\Theta/T)$ is the Debye function) we obtain an X-ray Debye temperature $\Theta^M=169$ (3) K. This is considerably lower than the values $\Theta^C=192$ (5) K and 200 (1) K obtained by Rayne (1963) from low-temperature heat capacity

Table 2. *Structure factors, extinction corrections and TDS correction factors*

h k l	$\lvert F_o\rvert$	$\sigma(F_o)$	$\lvert F_c\rvert$	$y^{1/2}$	t
2 2 0	8·250	0·005	8·233	0·7419	0·005
4 0 0	7·785	0·009	7·763	0·7968	0·013
4 2 2	7·363	0·012	7·321	0·8297	0·022
4 4 0	6·900	0·012	6·904	0·8524	0·032
6 2 0	6·391	0·008	6·510	0·8733	0·042
4 4 4	6·237	0·020	6·141	0·8856	0·053
6 4 2	5·841	0·008	5·791	0·8984	0·063
8 0 0	5·364	0·010	5·458	0·9113	0·073
6 6 0	5·080	0·010	5·151	0·9184	0·083
8 2 2	5·167	0·010	5·148	0·9219	0·083
1 1 1	2·796	0·009	2·910	0·9338	0·001
3 1 1	2·764	0·006	2·755	0·9564	0·008
3 3 1	2·598	0·007	2·594	0·9676	0·017
3 3 3	2·543	0·012	2·481	0·9732	0·026
5 1 1	2·433	0·007	2·455	0·9734	0·026
5 3 1	2·325	0·005	2·336	0·9773	0·036
5 3 3	2·239	0·008	2·166	0·9814	0·046
5 5 1	2·085	0·008	2·061	0·9837	0·057
7 1 1	2·101	0·007	2·083	0·9840	0·057
5 5 3	2·042	0·008	2·011	0·9847	0·067
7 3 1	1·982	0·006	1·951	0·9861	0·067
7 3 3	1·875	0·008	1·894	0·9871	0·077
5 5 5	1·685	0·014	1·686	0·9893	0·087
7 5 1	1·776	0·006	1·775	0·9884	0·087
2 0 0	2·708	0·004	2·698	0·9420	0·002
2 2 2	2·511	0·004	2·531	0·9601	0·009
4 2 0	2·365	0·005	2·373	0·9722	0·018
4 4 2	2·121	0·007	2·089	0·9820	0·037
6 0 0	2·036	0·009	2·087	0·9819	0·037
6 2 2	1·982	0·008	1·958	0·9849	0·047
6 4 0	1·822	0·005	1·837	0·9871	0·058
6 4 4	1·646	0·008	1·618	0·9902	0·078
8 2 0	1·635	0·006	1·614	0·9906	0·078
6 6 2	1·547	0·008	1·517	0·9913	0·088

measurements and Testardi (1970) from elastic moduli at 4·2 K. A direct comparison between these results is inappropriate. Unfortunately the heat capacity data extend over too small a range to enable us to determine the minus-second moment of the frequency distribution; we are therefore unable to compare our result with the associated Debye temperature Θ^M_∞ (Barron, Leadbetter, Morrison & Salter, 1966).

Neglect of the TDS correction leads to an overestimation of the harmonic vibrational parameters (*i.e.* an underestimation of the Debye–Waller factors) by approximately 10%, as can be seen from Table 1.

The value of the third-order anharmonic vibrational parameter is $\beta_{Ga} = -2\cdot3\ (1\cdot2)\times10^{-12}$ erg Å^{-3}. A purely harmonic model ($\beta_{Ga}=0$) refined to an R value of 0·0116 without significant change in the values of the other parameters. By applying Hamilton's (1964) statistical test to the ratio of the R values we find that the hypothesis that $\beta=0$ can be rejected at the 5% level. In addition we note that the inequalities predicted on an anharmonic model, for pairs of reflexions which would have equal structure factors in the absence of the cubic term, are correct in all four cases: thus $F(333)>F(511)$, $F(551)<F(711)$, $F(553)>F(731)$ and $F(555)<F(751)$.

Our results for the thermal parameters of $AuGa_2$ may be compared with those obtained by Hollenberg & Batterman (1974) in a recent X-ray diffraction study. These authors measured the temperature dependence of the integrated intensities of 17 Bragg reflexions from 300 to 625 K. They were able to account for the temperature dependence by introducing an isotropic quartic term $\delta(u_1^2+u_2^2+u_3^2)^2$ into the potential function, equation (1). This term they combined with the harmonic thermal parameter α to give an effective parameter α'. However the contribution to α' of the quartic term is quite small (< 1%) at room temperature, and a direct comparison of our thermal parameters with theirs is in order.

The results of Hollenberg & Batterman (1974) at 298 K are

$$\alpha'_{Au}=3\cdot72\ (7)\times10^{-12}\ \text{erg Å}^{-2},\quad B_{Au}=0\cdot88\ (2)\ \text{Å}^2$$
$$\alpha'_{Ga}=3\cdot77\ (10)\times10^{-12}\ \text{erg Å}^{-2},\quad B_{Ga}=0\cdot867\ (20)\ \text{Å}^2$$
$$-\beta'_{Ga}=1\cdot58\ (21)\times10^{-12}\ \text{erg Å}^{-3}.$$

We are thus in perfect agreement over the identity (within experimental error) of the vibrational amplitudes of Au and Ga atoms in $AuGa_2$. While the uncertainty in our value of β_{Ga} is relatively large, the agreement with the result of Hollenberg & Batterman is also quite satisfactory. Hollenberg & Batterman achieved a high accuracy in the determination of β_{Ga} by using a method which involves the ratio of intensities of harmonically equal, odd-index reflexions (Mair & Barnea, 1971). This method leads to the cancellation of errors due to any uncertainty in the TDS correction.

The TDS correction is important, however, in the accurate determination of the Debye–Waller factors – both in our study and that of Hollenberg & Batterman. There is a difference of ~20% between the two experiments for the value of the mean Debye–Waller factor: this discrepancy is well outside the range of the combined uncertainties for the two experiments. We have shown explicitly that neglect of the relatively small TDS correction in our experiment leads to an underestimation of the Debye–Waller factors by 10% (Table 1). Even had we omitted the TDS correction entirely we would still obtain Debye–Waller factors 10% higher than those of Hollenberg & Batterman.

As Hollenberg & Batterman (1974) point out, the equality of the mean-square vibrational amplitudes for the two atomic species in a crystal with the fluorite-type structure is peculiar to $AuGa_2$. For a number of fluorites XY_2 and antifluorites YX_2 the ratio B_Y/B_X of the Debye–Waller factors (and hence of the mean-square vibrational amplitudes) is approximately 1·5. This is the case for CaF_2, SrF_2, BaF_2, Mg_2Sn and Mg_2Si. In the case of UO_2 the ratio is approximately 2:1, a result which follows from the assumption that the single-particle potentials of U and O include nearest-neighbour interactions only (Rouse, Willis & Pryor, 1968).

Hollenberg & Batterman (1974) also draw attention to the magnitude of the ratio $|\beta_Y|/\alpha_Y$, stating that it is half as large in $AuGa_2$ as in CaF_2, BaF_2, SrF_2 and Mg_2Si. This is not strictly accurate as the value obtained by Cooper & Panke (1970) for Mg_2Si, *viz.* $|\beta_{Mg}|/\alpha_{Mg}=0{\cdot}56$ Å^{-1}, is comparable with the value for $AuGa_2$: $|\beta_{Ga}|/\alpha_{Ga}=0{\cdot}42$ (4) Å^{-1} according to Hollenberg & Batterman (1974) or 0·8 (4) Å^{-1} according to our results. A similar value obtains for Mg_2Sn (Skelton, Lin & Rothberg, 1974) with $|\beta_{Mg}|/\alpha_{Mg}=0{\cdot}41$ Å^{-1}. It is clear, however, that the ratio $|\beta_Y|/\alpha_Y$ is in general considerably larger for the ionic fluorites than for the intermetallic fluorites, the range of values for the former extending from 1·0 Å^{-1} for BaF_2 (Cooper, Rouse & Willis, 1968) to 1·3 Å^{-1} for CaF_2 (Cooper & Rouse, 1971; Harvey & Prager, 1975) and UO_2 (Rouse, Willis & Pryor, 1968).

Mair (1974) has pointed out that the ratio $|\beta|/\alpha$ provides a measure of the strength of the bond between nearest neighbours for a tetrahedrally coordinated atom in the diamond or fluorite structure, since it is this bond which must be stretched to allow cubic anharmonic thermal vibration. Mair (1974) notes that the values of $|\beta|/\alpha$ for the diamond-type structures Si and Ge (0·3 Å^{-1} and 0.4 Å^{-1} respectively) are well below the corresponding ratios for the anions in the closely related (ionic) fluorites, and concludes that this indicates a much greater stability of the tetrahedral covalent bond in the diamond structure than of the largely ionic tetrahedral bond in the ionic fluorites.

The same arguments and conclusions apply to a comparison between the intermetallic fluorites and the ionic fluorites: the tetrahedral bond in the former class is more stable than in the latter. It is interesting in this regard to note that according to Wernick, Menth, Geballe, Hull & Maita (1969) the Au–Ga distance in $AuGa_2$ is ~0·2 Å less than the sum of the coordination-12 radii of the atoms, suggesting considerable covalent character of the bonds.

Finally, Table 1 demonstrates the equivalence of the Zachariasen (1967) and Becker & Coppens (1974*a*,*b*) extinction corrections in the present experiment. This equivalence is in contrast to the results obtained by Harvey & Prager (1975) in a neutron diffraction study of CaF_2, where it was found that the Becker & Coppens formalism was to be preferred. The distribution parameter g obtained for both the $AuGa_2$ crystal and the CaF_2 crystal is of the same order of magnitude (~10^4). However the domain radius r of the CaF_2 crystal is much larger than that of the $AuGa_2$ crystal: $\sim 1\times10^{-3}$ cm compared to 5×10^{-5} cm. We find that in $AuGa_2$ the extinction effects are relatively small (minimum value of $y=0{\cdot}55$) and primary extinction is completely negligible, whereas in CaF_2 the effects are severe (minimum value of $y=0{\cdot}18$) and, although secondary extinction predominates, primary extinction is no longer negligible.

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References

Barron, T. H. K., Leadbetter, A. J., Morrison, J. A. & Salter, L. S. (1966). *Acta Cryst.* **20**, 125–131.

Becker, P. J. & Coppens, P. (1974*a*). *Acta Cryst.* A**30**, 129–147.

Becker, P. J. & Coppens, P. (1974*b*). *Acta Cryst.* A**30**, 148–153.

Busing, W. R., Martin, K. O. & Levy, H. A. (1963). *ORFLS*: Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Cooper, M. J. & Panke, D. (1970). *Acta Cryst.* A**26**, 292–293.

Cooper, M. J. & Rouse, K. D. (1971). *Acta Cryst.* A**27**, 622–628.

Cooper, M. J., Rouse, K. D. & Willis, B. T. M. (1968). *Acta Cryst.* A**24**, 484–493.

Dawson, B. (1967). *Proc. Roy. Soc.* A**298**, 255–263.

Dawson, B., Hurley, A. C. & Maslen, V. W. (1967). *Proc. Roy. Soc.* A**298**, 289–306.

Elcombe, M. M., Cox, G. W., Pryor, A. W. & Moore, F. H. (1971). *Programs for the Management and Processing of Neutron Diffraction Data.* Report AAEC/TM578, Australian Atomic Energy Commission.

Fehlmann, M. (1968). Personal communication.

Hamilton, W. C. (1964). *Statistics in Physical Science.* New York: Ronald Press.

Harvey, G. G. & Prager, P. R. (1975). *Acta Cryst.* A**31**, 393–394.

Hollenberg, W. C. & Batterman, B. W. (1974). *Phys. Rev.* B**10**, 2148–2158.

Mair, S. L. (1971). Personal communication.

Mair, S. L. (1974). Ph. D. Thesis, Univ. of Melbourne.

Mair, S. L. & Barnea, Z. (1971). *Phys. Lett.* **35**A, 286–287.

Nilsson, N. (1957). *Ark. Fys.* **12**, 247–257.

Neutron Diffraction Commission (1972). *Acta Cryst.* A**28**, 357–358.

Rayne, J. A. (1963). *Phys. Lett.* **7**, 114–115.

Rouse, K. D. & Cooper, M. J. (1968). *A Computer Program for the Correction of Measured Integrated Bragg Intensities for First-Order Thermal Diffuse Scattering.* Report AERE-R5725, Atomic Energy Research Establishment, Harwell.

Rouse, K. D., Willis, B. T. M. & Pryor, A. W. (1968). *Acta Cryst.* B**24**, 117–122.

Schwartz, L. H. (1964). *Acta Cryst.* **17**, 1614–1615.

Skelton, E. F., Lin, S. T. & Rothberg, G. M. (1974). *Acta Cryst.* A**30**, 39–42.

Strock, H. B. & Batterman, B. W. (1972). *Phys. Rev.* B**5**, 2337–2343.

Testardi, L. R. (1970). *Phys. Rev.* B**1**, 4851–4853.

Walker, C. B. & Chipman, D. R. (1969). *Acta Cryst.* A**25**, 395–396.

Warren, W. W., Shaw, R. W., Menth, A., Di Salvo, F. J., Storm, A. R. & Wernick, J. H. (1973). *Phys. Rev.* B**7**, 1247–1263.

Wernick, J. H., Menth, A., Geballe, T. H., Hull, G. & Maita, J. P. (1969). *J. Phys. Chem. Solids*, **30**, 1949–1956.

Willis, B. T. M. (1963). *Proc. Roy. Soc.* A**274**, 134–144.

Willis, B. T. M. (1969). *Acta Cryst.* A**25**, 277–300.

Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558–564.