KREUTLE, M. & MEYER-EHMSEN G. (1969). *Phys. stat. sol.* **35**, K17.

MENADUE, J. F. (1972). *Acta Cryst.* A**28**, 1.

MEYER, G. (1966). *Phys. Letters*, **20**, 240.

MIYAKE, S., KOHRA, K. & TAKAGI, M. (1954). *Acta Cryst.* **7**, 393.

MORABITO, J. M. JR, STEIGER, R. F. & SOMORJAI, G. A. (1969). *Phys. Rev.* **79**, 638.

OHTSUKI, Y. H. (1966). *J. Phys. Soc. Japan,* **21**, 2300.

PINSKER, Z. G. (1953). *Electron Diffraction.* London: Butterworths.

RAITH, H. (1968). *Acta Cryst.* A**24**, 85.

SIEGEL, B. M. & MENADUE, J. F. (1967). *Surface Sci.* **8**, 206.

TOMPSETT, M. F. & GRIGSON, C. W. B. (1966). *J. Sci. Instrum.* **43**, 430.

YOSHIOKA, H. (1957). *J. Phys. Soc. Japan,* **12**, 618.

The X-ray Debye Temperature of Aluminum

BY R. E. DINGLE* AND E. H. MEDLIN

Department of Physics, University of Adelaide, Adelaide 5001, Australia

Accurate photographic X-ray intensities have been obtained for nearly all reflexions within the Mo $K\alpha$ limiting sphere for two single crystals of aluminum. These intensities have been used to give the X-ray Debye temperature, Θ_D, in the first part of an experimental determination of the electron-density distribution in solid aluminum. The results of this work show that $\Theta_D = 393 \pm 1\,°K$ at $293\,°K$, varying with temperature to $\Theta_D = 362 \pm 9\,°K$ at $559\,°K$. The Debye parameter is found to be $0.849 \pm 0.005\ \text{Å}^2$ at $293\,°K$.

Introduction

It is of course the electron distribution in an atom that is responsible for its physical and chemical properties. In the free atom it is relatively simple to calculate the electron wave functions, the electron distribution and the X-ray scattering factors, f. Agreement to 1% is obtained with absolute experimental results by Chipman & Jennings (1963) for X-ray scattering out to $s = \sin\theta/\lambda \simeq 0.4$ by the spherically symmetrical monatomic gases neon, argon, krypton and xenon, but this is not so for some monatomic metallic solids where differences of *ca.* 4% have been found between experimental and Hartree–Fock free-atom scattering factors for low-angle reflexions by Batterman, Chipman & de Marco (1961) and subsequently by other workers as discussed by Weiss (1966). Free-atom wave functions cannot be, and are not, valid for the solid state; it is of interest to know in what way the free-atom wave functions are modified by solid-state interactions and we have asked this question for aluminum.

Accurate absolute measurements have been made on a number of X-ray reflexions from aluminum by a number of workers (Batterman *et al.*, 1961; Bensch, Witte & Wölfel, 1955; De Marco, 1967; Järvinen, Merisalo & Inkinen, 1969, Raccah & Henrich 1969, 1970; Inkinen, Pesonen & Paakkari 1970); their results confirm a solid-state effect and suggest that this is due to a redistribution of the conduction electrons alone. On

the other hand, the enigma with aluminum is that, in order to account for the fact that the low-angle scattering factors are less than those calculated for the 10 neon-core electrons alone, an unlikely core electron redistribution is suggested (Weiss, 1966). In any case recent theoretical scattering factors obtained by Arlinghaus (1967) from solid-state wave functions based on augmented-plane-wave calculations of the $3s$, $3p$ and indeed $2p$ energy bands have left the dilemma unresolved. The present position is that no solid-state wave functions have yet been obtained that can account for the low-angle scattering factors of aluminum.

Further, the limitation of diffraction data in reciprocal space leads to uncertainties in charge-distribution information. Present uncertainties are such as to justify its more accurate determination from a greater number of reflexion data and we have obtained these to $\sin\theta/\lambda \simeq 1.4\ \text{Å}^{-1}$. Other workers have been able to meet the required accuracy of *ca.* $\pm 1\%$ in atomic scattering factors and to make comparisons between calculated and observed values in spite of uncertainties in the Debye parameter, B, and the X-ray Debye temperature, Θ_D, which specify the effect of temperature on the intensities of X-rays scattered from a material. To make such comparisons, either the calculated scattering factors are to be multiplied by $\exp(-Bs^2)$ or the experimental values are to be multiplied by $\exp(Bs^2)$. With the small range of $\sin\theta/\lambda$ (*ca.* $0.6\ \text{Å}^{-1}$) for the first nine reflexions, any reasonable Debye temperature may be assumed. Raccah & Henrich (1969) chose $\Theta_D = 387\,°K$ but, with their limited range of data, little error would have resulted from the use

---

* Present address: Defence Standards Laboratories, Woodville North 5012, South Australia.

even of the original Debye (1912) value of $\Theta_D = 396\,°K$. However, uncertainties in Θ_D can lead to substantial errors in the scattering factors at higher s values. For example, uncertainty between $\Theta_D = 387$ and $393\,°K$ has the consequences shown in Table 1.

Table 1. *Uncertain in the scattering factor*

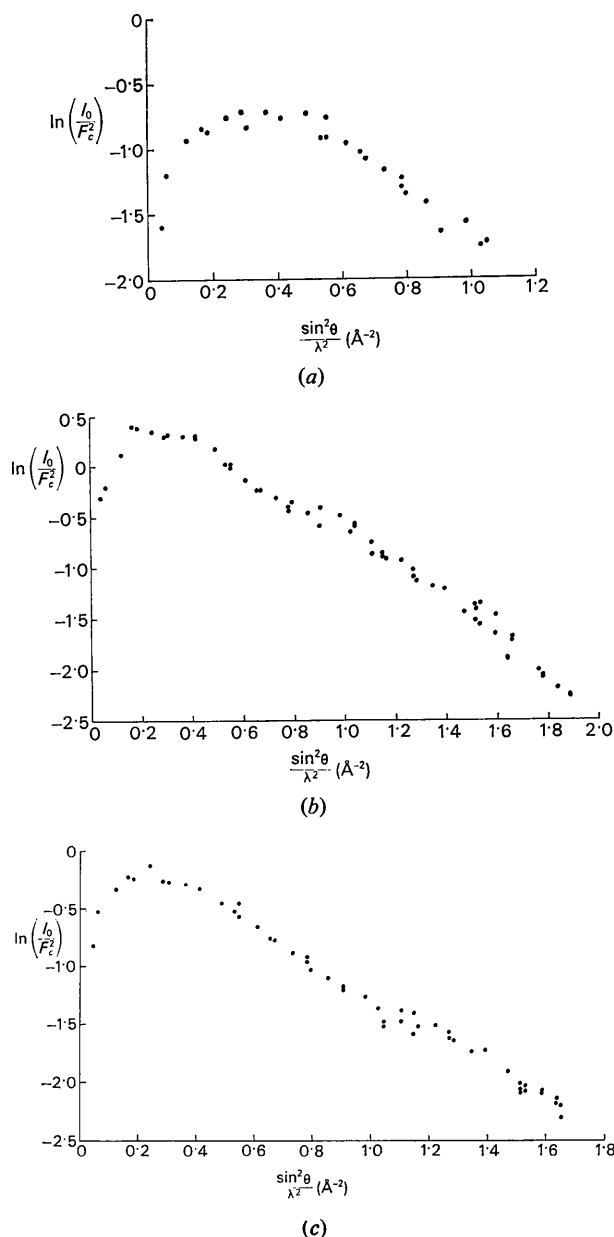| Reflexion	$\sin\theta/\lambda$	Uncertainty in scattering factor
(111)–1st	0·2139	0·2%
(422)–9th	0·6049	0·2%
(775)–58th	1·3694	0·8%

(a)

(b)

(c)

Fig. 1. Wilson plots (a) for intensity set 1a, (b) for intensity set 1b, (c) for intensity set 2.

If the maximum available experimental data is to be used for the determination of charge density by the Fourier transformation of the scattering factors, it is clearly important that B and Θ_D be accurately determined.

The results of previous experimental and theoretical determinations of Θ_D at room temperature are shown in Table 2.

Table 2. *Values of the X-ray Debye temperature for aluminum*

Author	Method	$\Theta_D(°K)$	$B(\text{Å}^2)$
James, Brindley & Wood (1929)	Single crystal	403	0·81
Owen & Williams (1947)	Powder	395	0·84
Chipman (1960)	Powder (A)	390 ± 10	0·87
	Powder (B)	407 ± 10	0·79
Flinn & McManus (1963)	Single crystal	410 ± 9	0·79
	Calculation	390	
Mothersole & Owen (1965)	Powder	397	0·84
De Marco (1967)	Single crystal	387 ± 2	0·89
McDonald (1967)	Single crystal (neutron data)	386 ± 10	0·89
	Calculation	390	0·87

All the values from experimental results are in some doubt because only the intensities of the scattered X-rays can be measured and these intensities depend upon $f^2 \exp\{-2Bs^2\}$; *i.e.* upon both f and B. Although other methods (Canut & Amoros, 1961) can be used for the determinations of B and Θ_D, it is customary to use methods that depend on one or other of the following assumptions.

(a) That the f's are sufficiently well known. Wilson (1942) type plots then yield a B value that is, at least in part, a consequence of the assumed f values.

(b) That the dependence of Θ_D and B on temperature is known. Intensity measurements made at two or more temperatures yield a B value that is, at least in part, a consequence of the assumed $B(T)$ (James, 1965).

We have attempted to minimize this fundamental difficulty by using method (a) to determine B from a series of intensity measurements at $\sin\theta/\lambda$ values in the range $0·2 < \sin\theta/\lambda < 1·4$, and confirming that a reasonable variation of Θ_D with temperature was then obtained from measurements at a range of temperatures. A preliminary account of this work has appeared (Median, Dingle & Field, 1969) and part of it is available in more detail elsewhere (Dingle, 1969).

Experimental

Two cylindrical single crystals (10 × 0·34 mm diameter) were selected from a batch of about 20 grown from 4N aluminum wire. The wire was annealed for 6 hours at

550°C, strained by 3%, and subjected to a travelling temperature gradient to 650°C for one hour. In the two crystals chosen, the lattice orientation was such that a [110] axis was within 10° of the cylinder axis in each case. The unit-cell size was taken to be 4·0494 Å (Swanson & Tatge, 1953).

Intensities of Zr filtered 40 kV Mo $K\alpha$ X-rays were recorded on five layers about [110] for each crystal by tin-interleaved multiple film pack equi-inclination Weissenberg photographs. For one crystal, independent sets of 28 and 58 symmetry independent reflexions were obtained, and 55 such reflexions were obtained for the other crystal. These are called sets 1a, 1b, and 2 respectively. Intensities were put on a relative scale by the visual estimation of 851 reflexions for set 1a, 1779 for set 1b and 1218 for set 2. That is, approximately 30 independent estimates were made of the intensity of each independent reflexion in each set. The usual corrections were made for film factor and interlayer scaling. Any intensity that departed from the mean value by more than 2 standard deviations was specifically checked for anomalies and, if thought necessary, rejected; in this way, about 70 intensity estimates were rejected. The maximum standard deviation in the distributions of intensities about their means was 10%, and the standard error of each estimated mean intensity is claimed therefore to be not greater than 2%.

Jeffery (1969) shows that a reflexion can be reliably recorded by the photographic method with an error of less than 1%, which is similar to the minimum error obtainable in counter measurements. The differences between the squares of structure factors for the same reflexion from similar crystals, however, are likely to be greater than this, and two crystals were used in the present study for this reason. The errors obtained for the photographic measurements in our work were also less than the 2→5% discrepancy between sets of structure intensities which was found by the A.C.A. project (Abrahams, Alexander, Furnas, Hamilton, Ladell, Okaya, Young & Zalkin, 1967), and hence no more accurate results would have been obtained by the use of monochromatic radiation and counters.

The relationship between the observed intensities and the scattering factors for aluminum is given by

$$(4f)^2 \exp\{-2Bs^2\} = KI(\mathrm{Lp})^{-1}H_D A(\mu,r)\,\frac{1}{1+\alpha} \qquad (1)$$

where

$I(hkl)$	is the observed intensity
$A(\mu,r)$	is the absorption correction
$(\mathrm{Lp})^{-1}$	is the Lorentz polarization correction
α	is the correction for thermal diffuse scattering (Willis, 1969)
H_D	is the anomalous dispersion factor
K	is a constant scaling factor
f	is the scattering factor at absolute zero [The structure factor $F(hkl)=4f(hkl)$]
μ	is the linear absorption coefficient.

Corrections were then made to the observed intensities for absorption by the cylindrical crystal (International Tables for X-ray Crystallography, 1959), for Lorentz polarization effects and for anomalous dispersion (James, 1965). Multiple diffraction was found not to have occurred. Corrections for primary and secondary extinction and for thermal diffuse scattering were not applied at this stage. Thus three sets of partly corrected intensity data had been obtained from two crystals.

Results

The processing of our results rests on the following assumptions:

(a) that experimental errors are known,
(b) that differences between the observed (F_o) and calculated (F_c) structure factors are real and due to solid state effects,
(c) that the F_c's will indicate necessary corrections to the F_o's but that they should not dominate such corrections.

Wilson plots using structure factors (F_c) calculated by Freeman & Watson (1961) from Hartree–Fock free atom wave functions for aluminum are shown in Fig. 1(a), (b) and (c) which were derived from intensity sets 1a, 1b and 2 respectively. The intensities for sin θ/λ >0·4Å⁻¹ for intensity sets 1b and 2 from different crystals both gave $B=0·86$ Å² which is in reasonable agreement with the earlier results given in Table 2, but the three sets of data used to give Fig. 1(a), (b) and (c) are shown by that Figure to have substantial extinction. Corrections were made following Darwin (1922) and Zachariasen (1963). Zachariasen (1967, 1968) has further developed the determination of extinction parameters but the principles are essentially those used here. In any case, the extinction parameters used were the mosaic block size, D, for primary extinction, and g and g', the coefficients which were used in the corrected value for μ in equation (1) when secondary extinction also occured. D, g and g' were treated
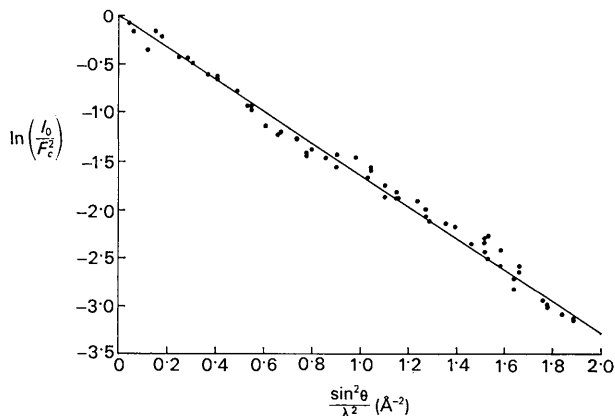

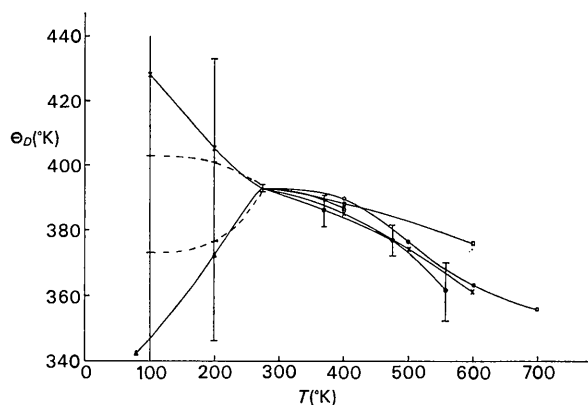Fig. 2. Wilson plot for intensity set 1b after correction for extinction.

Fig. 3. Variation of the Debye temperature with temperature for aluminum. × Chipman (1960), ●present work, △Flinn & McManus (1963), ○McDonald (1967), □Mothersole & Owen (1965).

as unknown although there has been some earlier work on these values for aluminum by Williamson & Smallman (1955), Kralina & Merezko (1964), and Kozlov & Kuznetsov (1968). Equation (1), modified for extinction but as yet ignoring thermal diffuse scattering, was solved for F_o by varying B, D, g and g' in such a way as to minimize the residue (Lipson & Cochran, 1953)

$$R_1 = \sum w(F_o - F_c)^2 \qquad (2)$$

where the weights, w, were obtained from the number of observations for the appropriate reflexion.

With R_1 minimized for each intensity set, the values of B were refined by using the difference electron density given by

$$\Delta\varrho(xyz) = \frac{1}{V} \sum (F_o - F_c) \cos 2\pi(hx + ky + lz) \qquad (3)$$

where the F_o values are those obtained from equation (1) with the extinction parameters that minimize equation (2). $\Delta\varrho(000)$ was plotted against a range of values of B and the value of B at the origin was found by interpolation (Lipson & Cochran, 1953). The F_o values so obtained were considered to be better estimates of the solid state structure factors than the calculated free-atom values. Accordingly, the free-atom F_c's were replaced by smoothed F_o values in order to minimize bias and the process repeated.

The final values of the extinction parameters are shown in Table 3.

The differences between the values for sets 1b and 2 containing 58 and 55 intensities respectively show the variation to be expected for different crystals. The differences for sets 1a and 1b containing 28 and 58 intensities respectively show the effect of determining the extinction parameters from a series of measurements over a smaller $\sin\theta/\lambda$ range for the same crystal. F_o values were obtained for each intensity set by using these extinction parameters in equation (1); and B values, which changed by less than 0·1% per cycle, were obtained from the difference synthesis as already described. The resulting Wilson graph for intensity set 1b is shown in Fig. 2 and it can be seen from this that the corrected intensities give a much more reliable B value. In fact the slope of the best fit straight line gives $B = 0.821$ Å² which does not differ significantly from the B value obtained by the Fourier synthesis method in this case.

The B values to this stage are also given in Table 3. The quoted errors are maximized and were obtained by considering the estimated errors in the final intensities in equation (1) to be caused only by errors in B. The weighted average value is $B = 0.816 \pm 0.003$ Å² which corresponds to a Debye temperature of $\Theta_D = 401 \pm 1°K$ and a root-mean-square displacement of 0·102 Å for isotropic harmonic vibration.

The measured intensities had not been corrected for the influence of thermal diffuse scattering at this stage. This correction has an effect on the scattered intensities which is similar to that produced by a change in the Debye parameter. The intensity of thermal diffuse scattering had been measured by Walker (1956) for directions between Bragg reflexions but no measurements were available for Bragg reflexion directions. The method devised by Willis (1969) was used to correct the measured intensities. The intensities of Bragg scattering were obtained by dividing the measured intensities by $(1 + \alpha)$ where

$$\alpha = \frac{8\pi}{3} \left(\frac{4\pi \sin\theta}{\lambda}\right)^2 \frac{q_{max}}{8\pi^3\varrho} KT^{\frac{1}{3}} \left(\frac{1}{V_l^2} + \frac{2}{V_t^2}\right). \qquad (4)$$

V_l is the longitudinal velocity and V_t is the transverse velocity of the acoustic modes of the lattice vibrations, and q_{max} is the maximum value of the magnitude of the wave vector for elastic waves which contribute to thermal diffuse scattering. The value of q_{max} was obtained from the average of the linear dimensions of the spots on the films (Annaka, 1962) which was 0·32 mm. Computed values of α for several reflexions from aluminum are shown in Table 4.

Table 3. *Final values of the extinction parameter*

Parameter	1a	Intensity set 1b	2
D	2.55×10^{-4}	5.99×10^{-3}	2.57×10^{-4}
g	4.4×10^5	2.46×10^5	2.17×10^5
g'	1.4×10^8	3.29×10^8	3.1×10^8
B	0.823 ± 0.007	0.817 ± 0.005	0.812 ± 0.005

Table 4. *Thermal diffuse scattering factors*

hkl	$\sin\theta/\lambda$ (Å⁻¹)	α
111	0.214	0.00299
400	0.494	0.0160
800	0.988	0.0636
775	1.369	0.123

The measured intensities were thus reduced by amounts which varied from approximately 0·3% to 12% in allowing for the effect of thermal diffuse scattering. The Debye parameters were only increased by approximately 0·03 Å^2 by this correction since $\alpha = 0·0652 \sin^2 \theta/\lambda$ and $1 + \alpha \simeq e^{\alpha}$ for small values of α. The sets of values of $F_0^2 \exp\{-2B \sin^2 \theta/\lambda^2\}$ which were obtained by using the above extinction parameters and the thermal diffuse scattering correction in equation (1) are given in Table 5.

Table 5. Final corrected intensities for each set of reflexions

hkl	Set 1a	Set 1b	Set 2	hkl	Set 1b	Set 2
111	1194	1175	992	822	11·5	11·1
200	1036	992	1166	660	10·3	10·4
220	721	608	677	751	9·68	10·2
311	535	597	565	555	9·93	8·81
222	444	536	503	662	9·31	8·97
400	324	333	374	840	8·33	8·17
331	268	275	260	911	7·38	7·19
420	214	250	239	753	6·79	7·37
422	185	180	183	842	6·43	6·82
511	146	151	146	664	5·89	5·92
333	144	150	148	931	5·32	5·53
440	114	103	102	844	4·13	4·34
531	83·2	78·3	81·3	933	4·06	3·67
600	91·4	70·5	85·4	771	3·63	3·54
442	79·1	74·2	75·4	755	4·25	3·81
620	64·0	52·3	57·0	10,00	4·27	3·56
533	53·1	42·8	46·8	860	3·39	3·66
622	47·6	41·6	44·5	10,20	3·64	3·32
444	39·1	34·6	35·1	862	2·98	3·23
711	33·1	27·7	30·8	951	2·32	2·97
551	30·9	26·7	29·4	773	2·55	2·90
640	28·7	27·7	26·4	10,22	2·77	2·30
642	23·6	22·1	21·5	666	2·93	2·60
731	17·4	21·5	18·4	953	1·93	2·09
553	17·4	18·5	18·4	10,40	1·79	2·19
800	16·5	18·2	15·3	864	1·84	2·17
733	12·8	14·1	12·5	0,42	1·59	
820	12·7	14·7	10·5	11,11	1·47	
644		14·8	11·1	775	1·45	

The final B values which were obtained by the above method from the three sets of corrected intensities are as follows:

Reflexion set	1a	1b	2
B	0·856 ± 0·010	0·850 ± 0·008	0·845 ± 0·008

The estimated error of ±10% in the determination of q_{max} in the thermal diffuse scattering correction caused an error of ±0·003 Å^2 in the final B value and this has been included in the above errors.

The average B value for the three sets of results was 0·849 ± 0·005 when the results for each reflexion set were given weights equal to the number of reflexions in the set. This value gave $\overline{(U_s^2)}^{1/2} = 0·104$ Å and $\Theta_D = 393 \pm 1\,°K$ at 293 °K for aluminum. This Θ_D value is comparable with the crude mean value of $\Theta_D = 397\,°K$ obtained from the exprimental results given in Table 1. The error of measurement is now much smaller and the value is more reliable because the result was derived from accurate intensity measurements over a wide range of $\sin \theta/\lambda$.

High-temperature measurements

As the value of B at 293 °K had been accurately determined it was possible to obtain reliable values of B at elevated temperatures from intensity measurements at two different temperatures. These results would also give an indication of the reliability of the room temperature B value as in method 'b' above.

The Debye parameter at a temperature T is related to the room temperature value B_0 by the equation

$$\ln \frac{I_T}{I_0} = -2(B - B_0)\frac{\sin^2 \theta}{\lambda^2} \tag{5}$$

where I_T and I_0 are the intensities of a reflexion from the crystal at temperature T and at room temperature respectively. A reflexion which had a small amount of extinction but gave a reasonable counting rate and a large change of intensity with temperature was selected viz. (511). Its intensity was measured at three elevated temperatures and room temperature using a proportional counter. The crystal was heated in a small cylindrical furnace divided into two sections to enable X-rays to pass through it; a maximum crystal temperature of 559 °K was attained.

Before and after the high temperature measurement, peak intensities were also measured at room temperature to safeguard against irreversible changes in crystallinity. Two suitable sets of measurements were obtained for each temperature and the results are given in Table 6.

The high temperature B values were obtained from the scattered intensities at pairs of temperatures by the use of equation 5 and the results are shown in Table 7.

The results for Θ_D vs. T and the corresponding error bars are shown in Fig. 3. The results of previous work adjusted to utilize $B = 0·849$ Å^2 at 293 °K are also shown and agreement within the error bars of the present work is seen for four of the sets of results.

Table 6. Count rates for high-temperature measurements

Experiment	I	II	III	IV	V	VI
Temperature (°K)	370	370	477	477	559	559
High temperature count rate (c.p.s.)	2957	2938	2091	1972	1462	1498
Room temperature count rate (c.p.s.)	3645	3536	3387	3269	3269	3452

Table 7. *High-temperature results*

Temperature (°K)	370	477	559
B (Å^2)	1·087	1·447	1·840
Θ_D (°K)	387 ± 5	378 ± 5	362 ± 9
Ratio error (%)	± 1·5	± 1	± 1·5
Temperature error (°)	± 2	± 3	± 9

Two sets of measurements giving widely different effects below room temperature have been made. These results after adjustment to utilize $B = 0·849$ Å^2 at 293 °K are also shown in Fig. 3. The error bars for a reasonable error of $2\frac{1}{2}$% in the intensity measurements (see Abrahams *et al.*, 1967) are also shown. The true value is expected to lie between the dashed lines and thus follow the trend observed for the values at elevated temperatures.

Conclusions

A more accurate value of Θ_D with a small reliably known error has been determined from a wide range of measurements on two single crystals. This has enabled the variation of Θ_D above room temperature to be accurately determined for the first time with known errors, and two previously different low-temperature results to be reconciled.

The work shows that although earlier estimates of B are satisfactory when discussing low-angle X-ray reflexions from aluminum, the more accurate value, which is reported here and which has been obtained from the experimental data, is required for making comparisons between calculated and observed scattering factors at high angles of reflexion. Such comparisons show that at $\sin\theta/\lambda = 0·9$ and $1·2$ Å^{-1} differences between free-atom and observed scattering factors are of the order of $+3$ and -5% respectively. Finally, we have obtained an empirical amplitude for the composite wave function of the $3s$ and $3p$ valence electrons in solid aluminum from the measured structure factors. This work is to be published.

References

ABRAHAMS, S. C., ALEXANDER, L. E., FURNAS, T. C., HAMILTON, W. C., LADELL, J., OKAYA, Y., YOUNG, R. A. & ZALKIN, A. (1967). *Acta Cryst.* **22**, 1.

ANNAKA, S. (1962). *J. Phys. Soc. Japan*, **17**, 846.
ARLINGHAUS, F. J. (1967). *Phys. Rev.* **153**, 743.
BATTERMAN, B. W., CHIPMAN, D. R. & DE MARCO, J. J. (1961). *Phys. Rev.* **122**, 68.
BENSCH, H., WITTE, H. & WÖLFEL, E. (1955). *Z. Phys. Chem.* **4**, 65.
CANUT, M. L. & AMOROS, J. L. (1961). *Proc. Phys. Soc.* **77**, 712.
CHIPMAN, D. R. (1960). *J. Appl. Phys.* **31**, 2012.
CHIPMAN, D. R. & JENNINGS, L. D. (1963). *Phys. Rev.* **132**, 728.
DARWIN, C. G. (1922). *Phil. Mag.* **43**, 800.
DEBYE, P. (1912). *Ann. Phys.* **39**, 789.
DE MARCO, J. J. (1967). *Phil. Mag.* **15**, 483.
DINGLE, R. E. (1969). Ph. D. thesis, Univ. of Adelaide.
FLINN, P. A. & MCMANUS, G. M. (1963). *Phys. Rev.* **132**, 2458.
FREEMAN, A. J. & WATSON, R. E. (1961). *International Tables for X-ray Crystallography*, Vol. III. Birmingham: Kynoch Press.
INKINEN, O., PESONEN, A. & PAAKKARI, T. (1970). *Ann. Acad. Fenn.* A. VI, *Physica*, p. 344.
International Tables for X-ray Crystallography (1959). Vol. II. Birmingham: Kynoch Press.
JAMES, R. W. (1965). *The Optical Principles of the Diffraction of X-rays*. London: Bell.
JAMES, R. W., BRINDLEY, G. W. & WOOD, R. G. (1929). *Proc. Roy. Soc.* A**125**, 401.
JÄRVINEN, M., MERISALO, M. & INKINEN, O. (1969). *Phys. Rev.* **178**, 1108.
JEFFERY, J. W. (1969). *Acta Cryst.* A**25**, 153.
KOZLOV, O. & KUZNETSOV, A. (1968). *Sov. Phys. Cryst.* **12**, 544.
KRALINA, A. A. & MEREZKO, N. F. (1964). *Fiz. Met. Metallov.* **18**, 56.
LIPSON, H. & COCHRAN, W. (1953). *The Determination of Crystal Structures*. London: Bell.
MCDONALD, D. L. (1967). *Acta Cryst.* **23**, 185.
MEDLIN, E. H., DINGLE, R. E. & FIELD, D. W. (1969). *Nature, Lond.* **224**, 581.
MOTHERSOLE, N. & OWEN, E. A. (1965). *Brit. J. Appl. Phys.* **16**, 1113.
OWEN, E. A. & WILLIAMS, R. W. (1947). *Proc. Roy. Soc.* A**188**, 509.
RACCAH, P. M. & HENRICH, V. E. (1969). *Phys. Rev.* **184**, 607.
RACCAH, P. M. & HENRICH, V. E. (1970). *Int. J. Quant. Chem.* III **5**, 797.
SWANSON, H. E. & TATGE, E. (1953). *Nat. Bur. Stand. U. T. Circ.* 539, VI.
WALKER, C. B. (1956). *Phys. Rev.* **103**, 547.
WEISS, R. J. (1966). *X-ray Determination of Electron Distributions*. Amsterdam: North Holland.
WILLIAMSON, G. K. & SMALLMAN, R. E. (1955). *Proc. Phys. Soc.* (B), **68**, 577.
WILLIS, B. T. M. (1969). *Acta Cryst.* A**25**, 277.
WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 152.
ZACHARIASEN, W. H. (1963). *Acta Cryst.* **16**, 1139.
ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558.
ZACHARIASEN, W. H. (1968). *Acta Cryst.* A**24**, 212.