

Take one of the non-zero column vectors as an eigenvector of the largest eigenvalue. The eigenvalue itself may be found by applying the original matrix to such a vector, and computing the ratio of the lengths. It should be noted that the multiplication by the matrix corresponds precisely to a shift generated by taking the derivative for least-squares refinement of unit vectors to the desired plane. One may test for uniqueness of the eigenvector by finding the components of the remaining non-zero column vectors of the matrix perpendicular to the one chosen.

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## The Debye–Waller Factor of Lead from 296 to 550 K

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The Debye–Waller factor of lead has been measured by neutron diffractometry at five temperatures in the range 296–550 K. The results are analysed in terms of a central-force pair-interaction model, and the anharmonic pair potential obtained is significantly different from that derived from previous X-ray measurements. Several methods of calculating TDS contributions to powder diffraction peaks are examined, and their results are compared.

### 1. Introduction

In a recent study of the X-ray Debye temperatures  $\Theta_D(T)$  of cubic materials, Killean (1974) has shown that the variation of the Debye–Waller factor,  $B(T)$ , of aluminum with temperature  $T$  can be adequately described by nearest-neighbour central-force (NNCF) pair interactions. This work has been extended to other f.c.c. metals (Killean & Lisher, 1975*a*), and to elastic-constant Debye temperatures of f.c.c. and b.c.c. elements (Killean & Lisher, 1975*b*). In all cases good agreement was found between theoretical predictions and the experimental data. A new criterion for melting was proposed (Killean & Lisher, 1975*b*) and this criterion, when applied to the elastic-constant data, yielded excellent agreement with the observed melting temperatures for the majority of materials studied. This melting criterion, however, was less successful when used with the X-ray data and it was not clear whether this was due to errors inherent in the X-ray measurements, or to shortcomings in the proposed theory. To resolve this point, a series of neutron diffraction studies of f.c.c. heavy metals is being undertaken, and the first of these experiments is reported in the present paper.

The neutron diffraction technique has several advantages over the X-ray method as a means of measuring absolute Debye–Waller factors. In the X-ray case there are problems such as uncertainties in the atomic

scattering factors, extinction and specimen misalignment which prevent an accurate determination of  $B(T)$  directly from the slope of a 'Wilson plot' of  $\ln I$  against  $\sin^2 \theta/\lambda^2$ . Several methods of minimizing the errors in the X-ray technique have been proposed, but these generally presuppose the knowledge of a relation between  $\Theta_D(T)$  and  $T$  and are thus unsatisfactory as a means of determining absolute Debye temperatures.

A Wilson plot may be used in the analysis of neutron diffraction data from powder samples, since the constancy of nuclear scattering lengths and the elimination of significant extinction in the specimen remove two principal sources of error which are  $\theta$ -dependent. A major drawback of the powder technique is the possibility of preferred orientation, and subsequent large changes in the orientation of the grains due to sintering at high temperatures. This effect may be reduced by annealing the powder before performing the diffraction measurements with the sample rotating or oscillating.

### 2. Experimental

The sample used in the present study was lead powder, of maximum particle size 150  $\mu\text{m}$  and purity 99.999%, which was obtained commercially from Goodfellow Metals Ltd. During the diffraction measurements this powder was contained in an aluminum can of diameter 16 mm and wall thickness 0.25 mm.

The neutron diffraction data were collected on the Curran powder spectrometer at AERE Harwell. In order to optimize the neutron flux and to facilitate the TDS corrections, faster-than-sound neutrons of wavelength 1.3649 Å were utilized. The maximum  $2\theta$  angle on the Curran is  $110^\circ$ , and this restricted to ten the number of reflexions that could be measured at each temperature. The use of a shorter wavelength would have theoretically made it possible to measure more reflexions, but the large  $B$  factors at high temperatures severely restricted the range of  $\sin \theta/\lambda$  over which it was feasible to record intensities.

A standard powder furnace was used to heat the can and sample, and data were measured at the temperatures, 296, 396, 445, 495 and 550 K. The background scattering from the empty can and furnace was also recorded at room temperature. A chromel–alumel thermocouple, situated at the base of the aluminum can, was used to determine the temperature, and measurements indicated a 10 K temperature gradient between the top and base of the can at 550 K. The furnace was stable to  $\pm 1$  K during all the powder runs made.

The reflexions were generally measured to a statistical accuracy of 1% although, at the higher temperatures, the reflexions at high  $\theta$  were only measured to within 5% because of the limited amount of instrumental time available.

The furnace and sample were kept stationary during the diffraction measurements but, at each temperature, a test was made for evidence of significant preferred orientations in the specimen. The furnace was rotated through an angle of  $90^\circ$  in steps of  $30^\circ$ , and the intensities of some low-angle peaks were recorded at each step. The results showed that the intensities of the reflexions were, within the statistical accuracy of the measurements, independent of the specimen angle, and this was taken to be a strong indication that preferred orientation was negligible.

### 3. Analysis of results

An analysis of the background scattering from the furnace and aluminum can indicated that the 222 peak from the lead was severely affected by overlap with the strong 220 aluminum reflexion. Owing to the uncertainty of the aluminum contribution at high temperatures it was decided to omit the 222 reflexion from the subsequent analysis. The 422 lead peak was also overlapped with an aluminum peak (400) but the latter, being very weak, did not introduce a significant error into the measured intensity of the lead reflexion.

Only the 331 and 420 peaks were unresolved and this doublet was analysed by a profile method, the peak shape being assumed to be Gaussian (Rietveld, 1969).

The integrated intensities were corrected for multiplicity and the Lorentz factor, but absorption corrections were not necessary. The values of  $B(T)$  determined from the data before the application of TDS corrections are given in column 2 of Table 1.

Table 1. Debye–Waller factors obtained from the Wilson plots

$\alpha_0$  refers to the data before correction for TDS. The TDS corrections denoted by  $\alpha_p$ ,  $\alpha_s$ ,  $\alpha_{wc}$  and  $\alpha_{awc}$  are described in the text. The  $B(T)$  values are accurate to  $\pm 0.05$  Å<sup>2</sup>.

$T$ (K)	$\alpha_0$ $B(T)$ (Å <sup>2</sup> )	$\alpha_p$ and $\alpha_s$ $B(T)$ (Å <sup>2</sup> )	$\alpha_{wc}$ $B(T)$ (Å <sup>2</sup> )	$\alpha_{awc}$ $B(T)$ (Å <sup>2</sup> )	Calculated $B(T)$ (Å <sup>2</sup> )
296	2.06	2.19	2.21	2.22	2.21
396	3.13	3.29	3.31	3.32	3.35
445	3.82	4.07	4.08	4.09	4.03
495	4.64	4.89	4.91	4.93	4.83
550	5.46	5.75	5.78	5.79	5.86

### 4. TDS corrections

As mentioned in § 2, the wavelength of the neutrons was chosen so that  $V_s \ll V_n$ . On theoretical grounds Willis (1970) and Cooper (1971) have shown that the TDS corrections for faster-than-sound neutrons are the same as the X-ray case, and recent high-resolution neutron time-of-flight studies by Steichele (1975) have confirmed these predictions. Thus in the present study it has been assumed that X-ray TDS corrections are applicable to the data.

Since lead is a highly anisotropic element with large  $B$  factors, the measurements afford a useful comparison between the various models which have been proposed for calculating TDS corrections to cubic powder diffraction data. These models may be split roughly into two groups, the first of which contains the isotropic models of Warren (1953), Paskin (1958, 1959) and Suortti (1967). In the isotropic approximation the velocities of sound in the material are assumed to be independent of crystallographic direction, and in the methods of Warren and Paskin the Debye lattice approximation is also invoked. Suortti (1967) extended the model by introducing dispersion, in the form of the linear chain, into each branch of the phonon spectrum. In the second group of models (Walker & Chipman, 1972) the anisotropy of the crystal is taken into account, and the polarization vectors and frequencies of the long-wavelength phonons are calculated separately for each direction.

Before it was possible to calculate TDS corrections by any of the above methods, it was necessary to obtain the values of the elastic constants of lead at the relevant temperatures. The only published measurements of  $C_{11}$ ,  $C_{12}$  and  $C_{44}$  appertain to the temperature range 0–300 K (Waldorf & Alers, 1962), and it has been necessary to extrapolate these results to higher temperatures using the analytical expressions relating  $C_{ij}$  as a function of  $T$  proposed by Varshni (1970).

TDS corrections have been calculated at each temperature by the following methods:

(1) The isotropic Debye model of Paskin (1959),  $\alpha_p$ , in which the transverse and longitudinal velocities of sound are treated separately;

(2) The isotropic model of Suortti (1967),  $\alpha_s$ , incorporating linear-chain dispersion;

(3) The anisotropic method of Walker & Chipman (1972);  $\alpha_{WC}$ , involving three-dimensional numerical integrations throughout the part of the Brillouin zone encompassed by the scan;

(4) The approximate anisotropic method of Walker & Chipman (1972),  $\alpha_{AWC}$ , which is based on a modified Debye model. The results for the 550K data are summarized in Table 2.

Table 2. TDS corrections to the data calculated by four methods

The corrections for the 222 reflexion are included for completeness, although this peak was omitted from the subsequent analysis.

<i>h k l</i>	$\alpha_p$ %	$\alpha_s$ %	$\alpha_{WC}$ %	$\alpha_{AWC}$ %
1 1 1	1.34	1.34	2.30	2.47
2 0 0	1.63	1.63	1.08	1.07
2 2 0	2.65	2.64	3.82	4.31
3 1 1	5.47	5.48	5.24	5.39
2 2 2	4.65	4.56	10.5	10.2
4 0 0	7.89	7.86	4.75	4.96
3 3 1	10.2	10.2	15.9	17.3
4 2 0	10.5	10.55	9.97	10.3
4 2 2	16.9	16.85	22.5	22.55
5 1 1				
3 3 3	22.7	22.7	23.2	24.2

Wilson plots were made from the data after correction for TDS by these four methods, and the values of  $B(T)$  obtained are given in Table 1. The isotropic methods of Paskin and Suortti produced almost identical results, and these models are incorporated in the same column. The Wilson plots of the  $\alpha_{WC}$  corrected data are shown in Fig. 1.

As can be seen from Table 2, there is little difference between the results of the two isotropic models  $\alpha_p$  and  $\alpha_s$ , showing that the corrections to these data are not significantly affected by the introduction of dispersion. This is consistent with the findings of Suortti (1967) that dispersion effects are only significant in the corrections applied to weak high-angle reflexions. The two anisotropic methods,  $\alpha_{WC}$  and  $\alpha_{AWC}$ , also produce results that are in good agreement showing that the approximate model proposed by Walker & Chipman can give accurate results for anisotropic materials with large  $B$  factors. This approximate method is several orders of magnitude faster on computing than the full anisotropic calculation, and its use is likely to be more widespread in future work.

The most interesting feature of Table 2 is the large difference between the results of the isotropic and anisotropic methods. In some cases the corrections vary by as much as 100% between the two types of models, and this would seem to emphasize the importance of allowing for anisotropy in all but the most isotropic materials. The  $B$  factors derived from the Wilson plots are, however, relatively insensitive to the method used in calculating the TDS corrections, as can be seen from Table 1. The difference in the  $B$  factors from the three

methods is always less than 1%, whereas the TDS corrections increase the  $B$  factors by approximately 6% of their uncorrected values.

### 5. The anharmonic pair potential

As stated in § 1 the results have been used in conjunction with the NNCF theory of Killean (1974). In this approximation the Debye temperature may be expressed in terms of the coefficients  $\alpha_2$  and  $\alpha_3$  in the expansion of the pair potential

$$\Phi(r) = \Phi(0) + \alpha_2 r^2 + \alpha_3 r^3 \quad (1)$$

between first nearest-neighbour atoms. For a f.c.c. lattice this relation is (Killean & Lisher, 1975a)

$$\Theta_D(T) = \Theta_D(0) \{1 + P_1[0.3409 \Theta_D(0) + T]\}^{1/2}. \quad (2)$$

In equation (1)  $r=0$  corresponds to equilibrium pair separation at 0K. In equation (2)  $\Theta_D(0) = 4(\alpha_2/M)^{1/2}$  and  $P_1 = 9\alpha_3^2 K_B/8\alpha_2^3$ , where  $K_B$  is Boltzmann's constant and  $M$  is the mass of an atom.

The equations relating  $B(T)$  and  $\Theta_D(T)$  are given by Killean & Lisher (1975a) equation (7), and they have been used with equation (2) to determine the values of  $\alpha_2$  and  $\alpha_3$  from the measured Debye-Waller factors. With the  $B$  factors derived from the  $\alpha_{WC}$  corrected data the following values were obtained:  $\alpha_2 =$

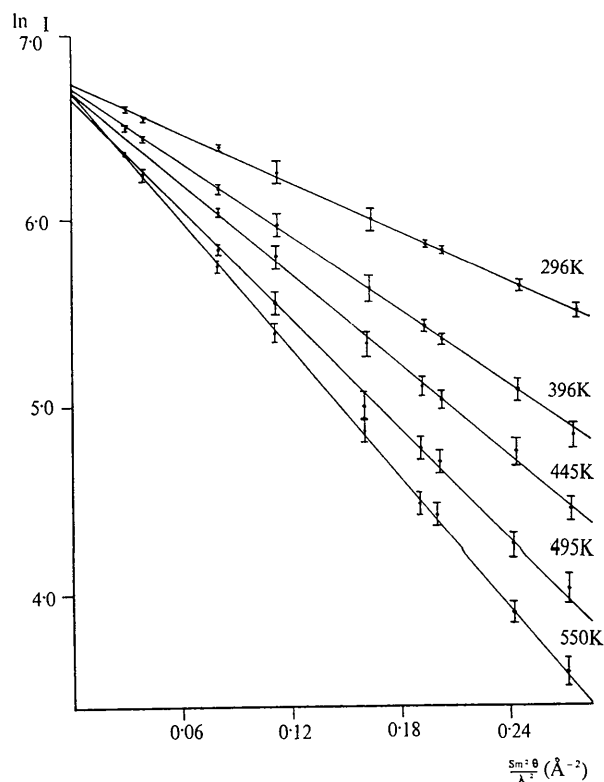


Fig. 1. Wilson plot of  $\ln I$  against  $\sin^2 \theta/\lambda^2$ . Data corrected for TDS by the method  $\alpha_{WC}$  of Walker & Chipman (1972). The least-squares straight lines weighted by  $1/\sigma^2$  are shown.

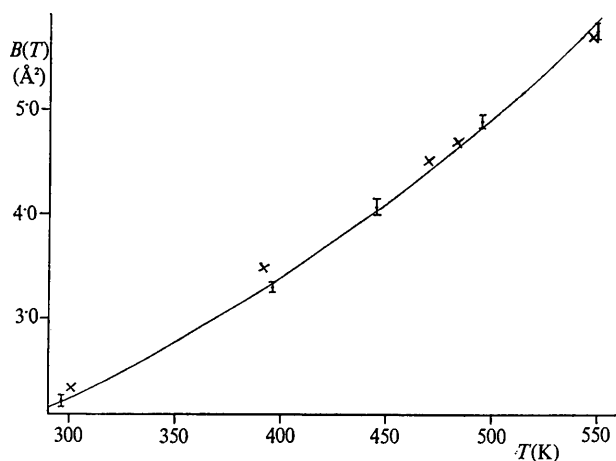


Fig. 2. The temperature dependence of  $B(T)$  for lead. The present neutron measurements are denoted by dots, and the X-ray results of Chipman (1960) by crosses. The continuous line represents the theoretical values calculated from equation (2).

$(3.81 \pm 0.09) \times 10^{-20} \text{JA}^{-2}$  and  $\alpha_3 = (-5.5 \pm 0.2) \times 10^{-20} \times \text{JA}^{-3}$ . The values of  $B(T)$  calculated from this pair potential are given in Table 1, column 6. The important factor, as concerns the melting criterion of Killean & Lisher (1975b), is the term  $\{8\alpha_2^3/9\alpha_3^2 K_B - 0.3409\Theta_D(0)\}$ , since this should be proportional to the melting temperature. Taking the above values of  $\alpha_2$  and  $\alpha_3$  this term is  $1143 \pm 40 \text{K}$ , considerably lower than the value of  $1256 \pm 35 \text{K}$  derived, from the X-ray measurements of Chipman (1960), by Killean & Lisher (1975a). It is, however, in good agreement with the value of  $1183 \pm 30 \text{K}$  obtained from the elastic constant data of Waldorf & Alers (1962) by Killean & Lisher (1975b), even though the values of  $\alpha_2$  and  $\alpha_3$  themselves, are smaller by 11% and 14%, respectively. It may be concluded, therefore, that the present results indicate a possible discrepancy between the interatomic pair potentials derived from X-ray and neutron diffraction measurements of  $B(T)$ . The results are plotted in Fig. 2.

## 6. Discussion

The intercepts on the  $\ln I$  axis in Fig. 1 serve as a critical test of the accuracy of the present results. For a particular Wilson plot, this intercept represents the

logarithm of the forward-scattered ( $\theta=0$ ) neutron intensity, and is thus independent of temperature. In Fig. 1 the intercepts of the five lines fall within one standard deviation of the mean value of 6.70.

In a recent paper Urban (1975) has investigated the influences of powder grain size upon X-ray TDS corrections. By considering the surface and edge vibrational modes, he has shown that the surface effects can be comparable with the usual volume scattering for very small grains ( $\approx 25 \text{Å}$ ), but these effects are only significant for grain sizes less than  $250 \text{Å}$ . Since the majority of neutron powder studies involve grain sizes in the order of  $1\text{--}100 \mu\text{m}$ , it is unlikely that surface scattering will ever be a large contribution to the TDS in these cases.

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