sities around the nuclei are totally unreliable without such a determination, in accordance with expression (3). The chemical interpretation of the density maps will be discussed in separate publications.

Conclusions

An estimate of the various errors indicates that scale factors can be measured with an accuracy of about 1%. Measurements using three methods agree within this error estimate.

Scale factors from conventional least-squares refinement are generally too large. Those obtained in a refinement with fixed neutron parameters are in better agreement with experimental values, but often somewhat low. Modified methods, such as refinement of high-order data, refinements with improved scattering factors, or refinements in which the shapes of the scattering factors are allowed to vary usually give scale factors in better agreement with the experimental scale factor, provided the accuracy of the data justifies such refinements. Such results should therefore be used instead of conventional scale factors in cases where experimental determinations of the absolute scale are impractical. However, a careful determination of the scale should be part of a charge density study, whenever feasible.

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X-ray Debye Temperature of Lead Nitrate

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The X-ray Debye temperature θ_M of lead nitrate has been determined to be 161 ± 6°K, by measurement of the temperature variation of the integrated intensities of Bragg reflexions from a powder specimen (method 1) in the temperature range 298–525°K. The room-temperature (298°K) Debye temperature for $Pb(NO_3)_2$ was determined to be 167 ± 6°K from integrated intensities of selected Bragg reflexions (method 2). Measured absolute structure amplitudes were used to calculate the root-mean-square displacements of the individual ions in $Pb(NO_3)_2$, which were found to be 0·713 ± 0·099 and 0·326 ± 0·046 Å for the Pb and $(NO_3)_2$ ions respectively.

1. Introduction

A number of physical parameters such as mean-square atomic displacements (Herbstein, 1961) and elastic constants (Gazzara & Middleton, 1964) are known to depend upon the Debye temperature of a solid. It has been shown by Salter (1965) that Debye temperatures obtained from different physical properties will not, in general, be equal. There is a scarcity of data on X-ray Debye temperatures in the literature, especially for the isomorphic nitrates of lead, barium and strontium.

In the present work, measurements of X-ray diffracted intensities at various temperatures were carried out with the object of extracting X-ray Debye temperature Θ_M for lead nitrate. The Θ_M obtained in the present investigation was compared with the previously reported Debye temperature Θ_D obtained from elastic constants (Michard, Plicque & Zarembowitch, 1973). An attempt has also been made to investigate the individual mean-square displacements for the individual ion types in $Pb(NO_3)_2$.

2. Theory

James (1967) has given in detail the general theory used in this work and the specific equations used have been taken from Walford & Schoeffel (1970). The slope of a plot of $\ln I$ *vs.* T can be used to derive the Debye temperature for any temperature using equation (6) of Walford & Schoeffel. Equation (4) of Walford & Schoeffel can be used to find an average Debye temperature for two widely separated temperatures.

A second method, which depends on the principle of measuring the integrated intensities of a large number of Bragg reflexions at a fixed temperature, was first outlined by Buerger (1960). Recently this method has been described in detail by Walford & Schoeffel (1970) and has been used here to determine the root-mean-square displacements of the individual ions.

3. Experimental

The powder sample of $Pb(NO_3)_2$ was obtained from British Drug Houses Ltd. London, and had a specified purity of 99·99 %. The powder (sieved to 44 μm particle size) was used for X-ray diffractometric studies. The experimental set-up used in this work is described elsewhere (Momin, Mathews & Karkhanavala, 1970).

Integrated intensities were measured using 2θ scans, β-filtered Cu $K\alpha$ radiation, and a pulse-height discriminator. The scan rates were adjusted so that the total net count for each method was the same ($\simeq 8\times10^3$). Scanning rates and background counting times were adjusted so that the statistical counting errors were less than 2 %. The integrated intensities of four reflexions were measured in the temperature range 298 to 525 °K, each measurement being repeated three times. The temperature of the sample was measured with a Pt–13 % Rh thermocouple with an estimated precision of ± 1 °K.

For method 2, the integrated intensities of eight to ten reflexions were measured at a fixed temperature (298 °K) and these measurements were repeated several times. The precaution was taken to minimize the extinction of using very fine powder samples.

4. Results

The measured intensities were corrected for thermal diffuse scattering (TDS) using the correction factor for cubic powders given by Chipman & Paskin (1959). In addition to TDS correction, intensities were also corrected for Lorentz–polarization (Lp) and absorption.

The corrected (TDS, Lp and absorption) intensities were used in equation (6) of Walford & Schoeffel (1970) to plot a graph of $\log I$ *versus* T for four reflexions of $Pb(NO_3)_2$. The graphs exhibit essentially the same behaviour, namely a straight line, and so the least-squares fittings were used to calculate the slopes. The Debye temperatures derived from these slopes are therefore average values over the temperature range 298–525 °K and values obtained for $\langle\Theta_M\rangle$ are given in Table 1. An alternative way of averaging the temperature dependence of Θ_M is through equation (4) of Walford & Schoeffel (1970) using $T_1=298$ °K and $T_2=525$ °K. These results are also given in Table 1. The standard deviations quoted in Table 1 are based solely on an estimated 3 % uncertainty in the measured intensities.

Table 1. *Debye temperatures calculated for various reflexions*

Those found by fitting least-squares straight lines to the log *I-vs.-T* plots are listed in column 4 and those found from ratios of intensities observed at the extreme temperatures are listed in column 5.

Compound	*hkl*	T(°K)	θ_M(°K)	θ_M(°K)
$Pb(NO_3)_2$	511	298–525	167 ± 6	161 ± 8
	440		150 ± 6	168 ± 8
	531		162 ± 6	170 ± 8
	600		165 ± 6	154 ± 8
	mean		161 ± 6	163 ± 8

The data for method 2 were collected at 298 °K. The plots of $\log (|F_{\text{corr}}|^2/|\sum f|)^2$ *vs.* $\sin^2\theta/\lambda^2$ for the even and odd-order reflexions are shown in Fig. 1. Here the symbol $|\sum f|^2$ stands for the calculated value of the square of the structure factor for lead nitrate. In calculating $\sum f$ the reliable positional parameters for all the atoms in the unit cell of $Pb(NO_3)_2$ were used from Wyckoff (1960). It is apparent from Fig. 1 that all the even-order reflexions lie on one straight line, and so do the odd-order ones. The solid lines in Fig. 1 are least-squares fits to the experimental data points. The Debye temperatures calculated from the slopes of the even-order and odd-order reflexions were, respectively, 167 ± 6 °K and 140 ± 6 °K. The root-mean-square (r.m.s.) displacements of Pb and $(NO_3)_2$ ions were estimated for even- and odd-type reflexions to be $0{\cdot}713\pm0{\cdot}099$ and $0{\cdot}326\pm0{\cdot}046$ Å respectively. These large uncertainties can be attributed to the sensitivity of the calculations to the measured intensities and to the lack of data for the odd-order reflexions.

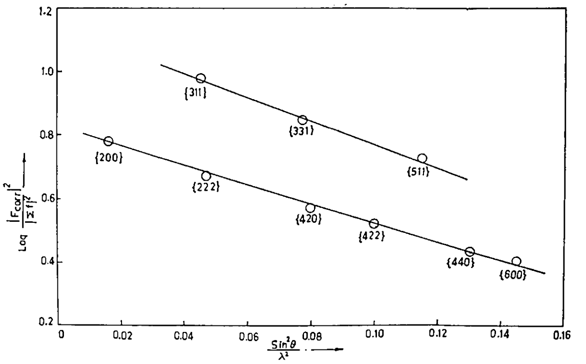

Fig. 1. Plot of log ($|F_{\text{corr}}|^2/|\Sigma f|^2$) *versus* $\sin^2\theta/\lambda^2$ for odd- and even-type reflexions from $Pb(NO_3)_2$.

5. Discussion

In the case of method 2, the Debye temperatures obtained from the even- and the odd-order reflexions differ from each other because they correspond to the individual Debye temperatures or mean-square atomic displacements appropriate to the two ions in each structure. This happens mainly because of the large mass difference between the two ions of $Pb(NO_3)_2$. The Debye temperature determined from the even-order reflexions is in good agreement with the results of method 1 within experimental errors. Whereas the Debye temperature obtained from the odd-order reflexions differs from method 1 by about $\pm 12\%$. Possibly this discrepancy in the case of odd-order reflexions may be attributed to the anharmonic atomic vibrations.

The value of Θ_M is found to be $162 \pm 7\,°K$ in the present work. This value of Θ_M compares very unfavourably with the value of 227°K, the previously reported Debye temperature Θ_D by Michard *et al.* (1973). It is found that $\Theta_M < \Theta_D$ (elastic constant value) for lead nitrate, which can be explained qualitatively on the basis of the frequency spectra. The acoustic and optic modes are well separated because of the fairly large mass difference [about 1·6:1 in $Pb(NO_3)_2$] between the two ion types. This separation of modes makes the X-ray Debye temperatures differ markedly from other Debye temperatures depending upon the frequency spectrum.

The r.m.s. displacements obtained for the individual ion types for $Pb(NO_3)_2$ are consistent with the respective ion masses. In HgSe (Walford & Schoeffel, 1970) and in PbTe (Keffer, Hayes & Bienenstock, 1970), the cation in both cases has larger mass and possesses displacements about twice as large as that of the anion. A similar phenomenon was observed in $Pb(NO_3)_2$, where the larger-mass cation (Pb) has a larger displacement in about the same ratio as that found in HgSe and PbTe.

The r.m.s. displacements for Pb and $(NO_3)_2$ ions differ significantly. Therefore similar measurements on isomorphous forms of barium and strontium nitrates would help in determining the dependence of the r.m.s. displacements on ionic masses.

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