

Debye-Waller factor of lead nitrate

R SOMASHEKAR, U D PRAHLLAD and M S MADHAVA

Department of Studies in Physics, University of Mysore, Mysore 570 006, India

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Abstract. The X-ray Debye-Waller factors and Debye temperatures of lead nitrate single crystals taken in the powder form have been determined by measuring integrated intensities of selected Bragg reflections at different temperatures. The characteristic specific Debye temperature has been compared with the value obtained from elastic constant data.

Keywords. Lead nitrate; Debye-Waller factor; Debye temperature.

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1. Introduction

In general, the thermal vibration of the atoms in a crystal primarily depends on the temperature, its mass and its surroundings; the way it is bonded to its neighbors. These effects cause the intensities of the Bragg reflections to decrease and this is referred to as the temperature factor or as the Debye-Waller factor. In the case of isotropic vibrations, a Debye temperature θ_M can be evaluated from such factors. The Debye temperature plays an important role in the understanding of a large number of solid state problems connected with lattice vibrations. Mean square atomic displacements (Herbstein 1961) and elastic constants (Gazzara and Middleton 1964) are known to depend on the Debye temperature of a solid. Methods of obtaining the Debye temperature involve different averaging procedures and exact agreement is not expected (Slater 1965).

Kulkarni and Bichile (1975) reported the room temperature Debye temperature (θ_M) for lead nitrate which was obtained by studying the variation of integrated intensities of reflections (511), (440), (531) and (600) and then using the extrapolation procedure of Walford and Schoeffel (1970) and it turned out to be 162 ± 7 K. Debye temperature (θ_M) obtained using elastic constant value, by Michard *et al* (1973) is 227 K. In the present work, we have determined the Debye-Waller factors at various temperatures by using all the available reflections and also the Debye temperatures from these data. We have also estimated specific heat Debye temperatures at various temperatures.

Measurements of X-ray diffraction intensities at seven different temperatures for lead nitrate were carried out with the object of extracting the X-ray Debye temperature θ_M using the Debye model where one does not distinguish between the acoustic and the optical branches of the dispersion curves. The Debye temperature is given by the

expression

$$B = \frac{6h^2}{pm_a k_B \theta_M} \left(\frac{\phi(x)}{x} + \frac{1}{4} \right) \quad (1)$$

where $\phi(x) = 1/x \int_0^x y dy / [\exp(y) - 1]$ and $x = \theta_M/T$, p is the number of groups, m_a is the mean molecular weight, k_B is the Boltzmann constant, h is the Planck constant and T is the absolute temperature.

Using the Debye-Einstein model where we have a Debye temperature and an Einstein temperature, the expression for B is

$$B = \frac{6h^2}{pm_a k_B \theta_M} \left(\frac{\phi(x)}{x} + \frac{1}{4} \right) + \frac{2(p-1)b^2}{pm_a k_B \theta_E} \left(\frac{1}{\exp(x_E) - 1} + \frac{1}{2} \right). \quad (2)$$

In the classical limit, both have the same linear dependence and separation of these two temperatures is not possible, but it has been observed that Einstein temperature should be $2^{1/2}$ times smaller than θ_M .

2. Experimental

Lead nitrate [$\text{Pb}(\text{NO}_3)_2$] is cubic with space group $T_h^6(\text{Pa}3)$ (Wyckoff 1951) and the substance decomposes at 743 K (Weast *et al* 1964). Colourless single crystals of lead nitrate were powdered and then used for recording the X-ray diffractometer at seven different temperatures viz., 299 and 373 to 673 (in steps of 50 K). Since it decomposes at 743 K, we could not record at a temperature nearer to 743 K. The uniformity of the temperature throughout the volume of the powdered sample was within ± 5 K. In all these recordings at various temperatures, it was found that the reflections from the planes (111), (200), (220), (311), (222), (400), (331), (420), (422), and (333) were present. For recording the diffractograms, a 2θ scan with a goniometer speed of 2° per min with the following specifications was adopted: 35 kV, 15.0 mA, chart speed 40 mm/min, channel width 50, channel centre 100, range 400 and time constant 2. X-ray intensities can be affected by the surface roughness and porosity of the sample. However the error due to this factor is about 2% at $2\theta = 20^\circ$ and is less at higher angles (Subhadra and Sirdesmukh 1977). The relative intensities were recorded over a 2θ range of 2° on either side of a peak and the background was estimated by a straight line. The integrated intensities were corrected for dead time effects using the method suggested by Chipman and Paskin (1959).

3. Results and discussion

To a first approximation, let the Debye-Waller factor (B) for lead, nitrogen and oxygen be equal to one another, so that we can define a mean value of B for lead nitrate. With this approximation the integrated intensity for lead nitrate is given by

$$I = K L_p P \left(\sum f \right)^2 \exp(-2B \sin^2 \theta / \lambda^2). \quad (3)$$

Here K is a constant, L_p is Lorentz polarization factor, P the multiplicity factor, θ is the Bragg angle, λ is the wavelength of the X-rays and B is the mean Debye-Waller factor for lead nitrate $[\text{Pb}(\text{NO}_3)_2]$. The atomic scattering factors given in international table (1969) have been used to compute $(\Sigma f)^2$.

It follows from (3) that a graphical plot of $\ln(I/KL_pP|\Sigma f|^2)$ against $\sin^2 \theta/\lambda^2$ is a straight line and the least-squares method has been used to determine the slope and also the standard deviation from which the temperature factor B is obtained. Using this value in (1) and the published value of $W(x)$ for various x (Benson and Gill 1966), we have determined θ_M for the Debye model. θ_E for the Debye-Einstein model is given by $\theta_M/2^{1/2}$. The specific heat Debye temperature is given by $\theta_D = p^{1/2}\theta_M$, where p is the number of groups (Horning and Staudenmann 1988).

The present values of Debye-Waller factor, Debye temperature (θ_M) and θ_E are given in table 1 for different temperatures. $\theta_D - T$ plot for lead nitrate is given in figure 1. Using crystal data of lead nitrate at room temperature (Wyckoff 1951), the Debye temperature using the relation (Lindemann 1910)

$$\theta_{(\text{theoretical})} = C(T_m/M V^{2/3})^{1/2}, \quad (4)$$

Table 1. Debye-Waller factor and Debye temperature for lead nitrate.

Temperature (K)	$B(\text{nm}^2)$	Crystal data	θ_E Debye-Einstein model (K)	θ_M Debye model (K)
299	2.0 + 0.2	cubic	89.0	125.9
373	2.4 + 0.2	$a = 7.84 \text{ \AA}$	90.5	127.9
423	1.8 + 0.2	—	110.7	156.5
473	2.6 + 0.1	—	98.7	139.5
523	3.5 + 0.1	—	88.8	125.5
573	4.0 + 0.3	—	86.3	122.0
623	4.9 + 0.1	—	81.5	115.3
673	5.3 + 0.1	—	81.4	115.1

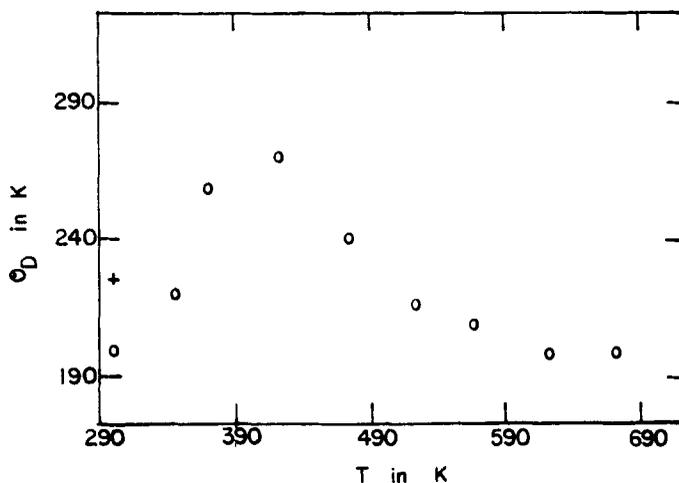


Figure 1. Variation of estimated specific Debye temperature with temperature. O - present result; + - θ_D estimated using elastic constant value (Michard *et al* 1973).

turns out to be 103 K. Here $C (= 115)$ (Lindemann 1910) is a constant dependent on the structure, T_m is the melting temperature, M is the mean molecular weight and V is mean molecular volume. The variation of θ_D with temperature is given in figure 1 along with reported value of θ_D obtained from elastic constant and there is a good agreement. From table 1 it follows that the Debye-Waller factor increases with increase in temperature. The theoretically estimated Debye temperature using (4) agrees with the Debye temperature obtained from the Debye model. In figure 1, θ_D as well as θ_M , at first, increases and then decreases with temperature. This curve falls into the general category of curves observed in cubic metals and also in halides (Blackmann 1955) and appears therefore to have no relation to bonding or to detailed crystal structure. The similarities are however due less to the crystal structure than to the similarities in the relative magnitudes of the forces between atoms or ions. The general conclusion is that there is no specific crystal structure effect on the $\theta_D - T$ curves.

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