approximated by adjusting these factors. The present work then provides a rapid means of calculating the absorption and the derivatives needed to estimate μR in the least-squares procedure. Equation (1) may be rearranged to give

$$\frac{dA^*}{d\mu R} = \frac{\bar{T}A^*}{R}$$

which can be computed as a function of $\sin\theta$ with (6).

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An X-ray diffraction study of lithium.

By B. BEDNARZ and D. W. FIELD*†, Physics Department, University of Adelaide, South Australia

Abstract

An accurate X-ray diffraction investigation has been carried out on two single crystals of lithium. The data from crystal 1 were obtained at temperatures of 248 and 296 K, and those for crystal 2 in the temperature range 293 to 423 K. The measured integrated intensities have been analysed for the presence of anharmonicity in the atomic vibrations by using a temperature factor based on a one-particle potential of the form $V(u) = \frac{1}{2}au^2 + \gamma u^4 + \delta(u_x^4 + u_y^4 + u_z^4 - \frac{3}{5}u^4)$. An average value for the parameter δ of 290 ± 140 eV nm^{-4} was found. No significant value of γ was found in the analysis of data from crystal 1, but a value of −360 ± 40 eV nm^{-4} was obtained from the higher-temperature data of crystal 2.

Introduction

Previous results on the analysis of accurate X-ray diffraction data for anharmonic features in the Debye–Waller factor have been given for sodium by Field & Medlin (1974) and Field & Bednarz (1976), and for potassium by Bednarz & Field (1982). Here we present results of a final experiment on lithium.

Experimental

Two crystals of 99.95% pure material were prepared according to the method of Bednarz (1977). Intensities were recorded from crystal 1 at 248 K, but while doing so a sudden permanent change in the mosaic spread occurred. Thus two independent data sets were collected at each of the temperatures 248 and 296 K, one being characterized by small isotropic mosaic spread, and hereafter referred to as

data subset 1B, and the other by a large anisotropic mosaic spread, hereafter referred to as data subset 1A. An attempt to record data at 200 K destroyed the crystal. The intensities of 17 independent reflections were recorded from crystal 2 at 293 K and the temperature dependence of one 220 reflection was measured in the range 293 to 423 K.

Analysis

The theory and methods of analysis were generally as detailed in Bednarz & Field (1982), hereafter referred to as paper I. In particular, equation (2) in I is the expression used for the temperature factor for the one-particle-potential model for lithium.

Two models were used in the data analysis. In model 1, it was assumed that the potential parameter γ in equation (2) of I was zero, while in model 2, γ was allowed to vary. The value of the Gruneisen constant γ_G was taken from Martin (1965) to be 0·86 and the volume coefficient of expansion χ_v was taken from Kittel (1971) to be 135 MK^{-1}.

Results

The subsets 1A and 1B of the data from crystal 1 were analysed independently for each of the temperatures 248 and 296 K. With model 1, consistent results were obtained for all the parameters except δ, for which a range of 190 + 110 to 460 ± 80 eV nm^{-4} was obtained. The agreement between refined and measured scale factors was excellent. Average values for the potential parameters from these refinements are listed in Table 1. In this table, a_{293} represents the value of a at 293 K and $u_{\text{r.m.s.}}$ is the root-mean-square vibration amplitude determined by

$$u_{\text{r.m.s.}} = \left(\frac{3k_BT}{a}\right)^{\frac{1}{2}}.$$

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Table 1. *Average values for parameters refined with model 1 from data from crystal 1*

α_0	$45 \cdot 3 \pm 0 \cdot 4$ eV nm^{-2}
δ	360 ± 120 eV nm^{-4}
α_{293}	$42 \cdot 2 \pm 0 \cdot 3$ eV nm^{-2}
$u_{r.m.s.}$ at 293 K	$0 \cdot 0424 \pm 0 \cdot 0001$ nm

Table 2. *Parameters refined from data for crystal 2*

	293 K data subset Model 1	Full data set Model 2
α_0 (eV nm^{-2})	$45 \cdot 3 \pm 0 \cdot 2$	$45 \cdot 9 \pm 0 \cdot 3$
α_{293} (eV nm^{-2})	$42 \cdot 2 \pm 0 \cdot 2$	$42 \cdot 8 \pm 0 \cdot 3$
γ (eV nm^{-4})	$0 \cdot 0$	-360 ± 40
δ (eV nm^{-4})	200 ± 100	130 ± 120
$u_{r.m.s.}$ at 293 K (nm)	$0 \cdot 0424 \pm 0 \cdot 0001$	$0 \cdot 0421 \pm 0 \cdot 0002$
Level at which δ significant	$0 \cdot 25$	not significant
Level at which γ significant	–	$0 \cdot 005$

An extension of the analysis for each of the data subsets from crystal 1 by the use of model 2, in which the isotropic potential parameter γ was allowed to vary, did not produce a value of γ significantly different from zero.

The data obtained from crystal 2 consisted of 17 independent reflections, the intensities of which were measured at 293 K (referred to as the '293 K subset') and a further 13 measurements of the 220 reflection at temperatures from 293 K in steps of 10 K to 423 K. The parameters refined for the 293 K subset of data and the complete data set from crystal 2 are given in Table 2. The entries 'level at which δ (or γ) significant' in Table 2 refer to that level, with Hamilton's (1965) R-factor ratio test, at which the change in R factor was significant on the introduction of the δ (or γ) parameter into the analysis.

Discussion

(a) The parameter δ

Although the evidence is not exceptionally strong, it does seem that there is a small but significant anisotropic anharmonic component in the one-particle potential for lithium. The average value obtained from all the refinements for the parameter δ is $\delta = 290 \pm 140$ eV nm^{-4}. The positive sign for the term is consistent with that found in the other alkali metals, sodium and potassium, and means that there is a greater probability of vibration of the atoms in the nearest-neighbour directions than in the next-nearest-neighbour directions. A possible explanation for this has been advanced in I.

(b) The parameter γ

As mentioned in *Results*, refinements with model 2, where γ was allowed to vary, gave no significantly better fits to the data for crystal 1 than did model 1. This would place a lower limit on the value of γ for lithium in the temperature range 248 to 296 K of about -400 eV nm^{-4} at the $0 \cdot 05$ significance level, with Hamilton's tables.

However, for the data from crystal 2, a value of $\gamma = -360 \pm 40$ eV nm^{-4} was found, significant at better than the $0 \cdot 005$ level. The sign of γ is consistent with an expected 'softening' of the vibrations and also with the sign observed in potassium (paper I). However, the result needs to be treated with some caution since it is largely due to higher temperature (> 293 K) data obtained from just one reflection. the 220 reflection. Nevertheless, the observed decrease in intensity cannot be ascribed to an increased value of the parameter δ at higher temperatures and, although the parameters α and γ are highly correlated, neither can the data be fitted by a quasiharmonic model for any value of the parameter α that is consistent with our other results, as can be seen in Fig. 1. In this figure. the quantity

$$-\frac{\lambda^2}{2 \sin^2 \theta} \ln\left(\frac{I_0}{k_s f_c^2}\right)$$

is plotted as a function of temperature for the intensities measured from the 220 reflection from 293 to 423 K. In the quasiharmonic approximation. the quantity plotted on the vertical axis is just the Debye parameter B. The solid line in the figure is the plot of the quasiharmonic temperature variation of B given by

$$B = \frac{8 \pi^2 k_B T}{\alpha}.$$

where

$$\alpha = \alpha_{293} \left[1 - 2\gamma_G \chi(T - 293) \right].$$

and α_{293} was taken as $42 \cdot 2$ eV nm^{-2}.

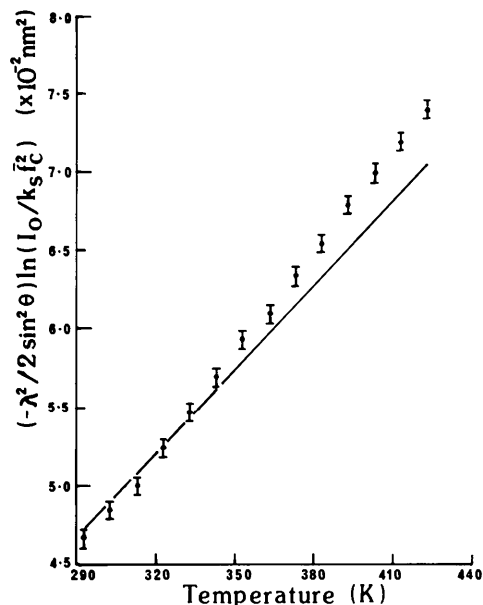However, it appears that at temperatures greater than the Debye temperature of 326 K (see below) the parameter γ

Fig. 1. Variation with temperature of $(-\lambda^2/2 \sin^2 \theta) \ln (I_0/k_s f_c^2)$ for the 220 reflection of lithium compared with the variation expected on the basis of a quasiharmonic model. Vertical bars represent errors of 1% in I_0.

becomes significant in describing the vibrational properties of the atoms of lithium.

(c) The parameter α

The agreement between all subsets of data analysed for the isotropic harmonic parameters α_0 and α_{293} is excellent. The mean values from all subsets are

$$\alpha_0 = 45 \cdot 3 \pm 0 \cdot 4 \text{ eV nm}^{-2}$$

and

$$\alpha_{293} = 42 \cdot 2 \pm 0 \cdot 3 \text{ eV nm}^{-2}.$$

Hence, the corresponding values of $u_{\text{r.m.s.}}$ and Debye temperature calculated from them must be considered to be very reliable. The root-mean-square displacement $u_{\text{r.m.s.}} = 0 \cdot 0424 \pm 0 \cdot 0001$ nm. The Debye temperature θ_D is given by

$$\langle u^2 \rangle = \frac{9 \hbar^2 T}{M k_B \theta_D^2} \left[1 + \frac{1}{36} \left(\frac{\theta_D}{T} \right)^2 \right].$$

where M is the atomic mass. The value obtained was $\theta_D =$

326 ± 1 K. This may be compared with the value of 352 ± 12 K obtained by Pankow (1936).

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Six regular polygons at a four-connected vertex.

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Abstract

Six angles are formed between four straight lines meeting at a point in space. Since there is one relationship between them, only certain combinations of six regular polygons will fit together at such a point. Some of these are enumerated.

When four straight lines meet at a tetrahedral vertex in space they make six angles, any one of which is determined by the other five as the solution to a quadratic equation. The relationship between them was known to Carnot (1803) and was stated by Fedorov (1886) in the modern determinantal form:

$$\begin{vmatrix} 1 & \cos\theta_{12} & \cos\theta_{13} & \cos\theta_{14} \\ \cos\theta_{12} & 1 & \cos\theta_{23} & \cos\theta_{24} \\ \cos\theta_{13} & \cos\theta_{23} & 1 & \cos\theta_{34} \\ \cos\theta_{14} & \cos\theta_{24} & \cos\theta_{34} & 1 \end{vmatrix} = 0.$$

In dealing, for example, with network silicates, we can ask what combinations of six regular polygons may meet at such a tetrahedral vertex. The corresponding solutions for a vertex in a plane at which three regular polygons meet are quoted in Table 1 (from Holiday & Philpot, 1977).

The formula quoted derives from the metric matrix of a unit cell with four axes of unit length, the terms of the matrix being the scalar products $\mathbf{a}_i \mathbf{a}_j$ of all pairs of axes. The determinant of the metric matrix gives the square of the four-dimensional content of the unit cell. If the metric matrix

Table 1. The possible combinations of three regular polygons at a common vertex in the plane

If the number of sides of the polygon is given as negative it indicates that the corresponding polygon contains the other two.

(1–2)	(1–3)	(2–3)
3	7	42
3	8	24
3	9	18
3	10	15
3	12	12
4	5	20
4	6	12
4	8	8
5	5	10
6	6	6
3	3	−6
4	3	−12
5	3	−30