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Temperature Dependence of Thermal Vibrations in Lead as Determined from Short-Wavelength Neutron Diffraction Data

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Abstract

The temperature dependence of the atomic thermal motion in lead has been studied by analysis of diffraction measurements with 0·535 and 0·844 Å neutrons. Full single-crystal data sets were collected at ten temperatures ranging from 100 K to the vicinity of the melting point at 600 K. The data were interpreted in the anharmonic one-particle-potential formalism. Significant values for both isotropic and anisotropic quartic-anharmonic potential parameters were obtained, but a single temperature-independent one-particle potential was found sufficient to describe the temperature dependence of the atomic temperature factor only above $\sim 4\theta_M$, where θ_M is the Debye temperature.

Introduction

The temperature dependence of the atomic vibrations in lead has been subjected to two previous diffraction studies. Chipman (1960) measured the temperature dependence of the X-ray integrated intensity of the 511, 333 reflection in the temperature range 85–576 K using a powder sample and Cu $K\alpha$ radiation. The data were analysed in terms of the Debye temperature and evidence was found for an explicit temperature dependence of the Debye temperature beyond that resulting from the simple dependence on volume alone (quasiharmonic approximation). It was also suggested that a more exact treatment of the problem of anharmonicity is required for understanding the observations. Lisher (1976) determined the Debye–Waller factor of lead from the neutron diffraction data collected on a powder sample at five temperatures in the range 296–550 K. The data were interpreted in terms of an anharmonic pair potential (Killean, 1974) and a significant anharmonic contribution to the pair potential was found. Zarochentsev, Kravchuk & Tarusina (1976) calculated the mean-square amplitudes in lead in the temperature range from zero to the melting point making use of the model with a two-parameter Heine–Abarenkov pseudopotential. The calculations were carried out in the harmonic and quasiharmonic approximations. The intrinsic anharmonic contributions to the mean-square displacement at high temperatures were estimated using the approximation that the frequency shift is a linear function of temperature.

With the aim of obtaining independent insight into the development of the atomic thermal motion with temperature, diffraction measurements with short-wavelength neutrons were carried out on a single crystal at ten different temperatures ranging from 100 K to the vicinity of the melting point. The data collected at each temperature were analysed independently in the framework of the one-particle-potential formalism (Dawson, Hurley & Maslen, 1967; Willis, 1969; Willis & Pryor, 1975; Dawson, 1975) with the particular aim of establishing parameters for the description of the intrinsic anharmonic contributions to the atomic vibrations.

The OPP model

In the one-particle-potential (OPP) formalism the crystal is treated as a system of independent anharmonic oscillators. In the high-temperature limit of this model the thermal smearing function (or the probability density function) $t(\mathbf{u})$ is the Boltzmann distribution function

$$t(\mathbf{u}) = (1/N)\exp[-V(\mathbf{u})/k_BT];$$
$$N = \int \exp[-V(\mathbf{u})/k_BT]\,\mathrm{d}^3\mathbf{u}, \qquad (1)$$

where k_B is the Boltzmann constant, T is the absolute temperature and $V(\mathbf{u})$ is the OPP conventionally expanded in a power series in the Cartesian coordinates u_x, u_y, u_z of the atomic displacement $\mathbf{u}$. Following the notations of Willis (1969; Willis & Pryor, 1975),

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the appropriate site-symmetrized form to fourth order for the lead atom, which is located at a site of $m3m$ symmetry, is given by

$$V(\mathbf{u}) = \tfrac{1}{2}\alpha u^2 + \gamma u^4 + \delta(u_x^4 + u_y^4 + u_z^4 - \tfrac{3}{5}u^4), \qquad (2)$$

where α, γ and δ are the coefficients of the expansion, or the force constants. The corresponding atomic temperature factor $T(\mathbf{Q})$ is obtained by Fourier transforming $t(\mathbf{u})$. If the sum of anharmonic (fourth-order) terms in (2) is small compared with the harmonic (second-order) term, $T(\mathbf{Q})$ is given by the expression

$$\begin{aligned} T(\mathbf{Q}) = N \exp[-\tfrac{1}{2}Q^2k_BT/\alpha]\Big\{ & 1 - 15k_BT\frac{\gamma}{\alpha^2} \\ & + 10(k_BT)^2\frac{\gamma}{\alpha^3}Q^2 - (k_BT)^3\frac{\gamma}{\alpha^4}Q^4 \\ & - (k_BT)^3\frac{\delta}{\alpha^4}(Q_x^4 + Q_y^4 + Q_z^4 - \tfrac{3}{5}Q^4)\Big\}, \\ N = \left(1 - 15k_BT\frac{\gamma}{\alpha^2}\right)^{-1}, & \qquad (3) \end{aligned}$$

where Q_x, Q_y, Q_z are the Cartesian components of the diffraction vector $\mathbf{Q}$.

The mean-square displacement of an atom in this anharmonic OPP model is given by the expression

$$\begin{aligned} \langle u^2\rangle &= \textstyle\int u^2 \exp[-V(\mathbf{u})/k_BT]/\int \exp[-V(\mathbf{u})/k_BT] \\ &= N(k_BT/\alpha)(1 - 39k_BT\gamma/\alpha^2), \qquad (4) \end{aligned}$$

where N is the normalization factor defined above.

Experimental

The sample crystal is an approximately cubic single-crystal piece of 27.6 mm^3 gently cut to shape by a solubility saw. The neutron diffraction data were collected on the four-circle diffractometer D9 at the hot source of the Institut Laue–Langevin high-flux beam reactor. 12 sets of data were collected over the temperature range 100–593 K. The melting point of lead is 600·6 K. The data sets at the lower temperatures were collected with neutrons of wavelength 0·535 Å to ensure as many high-order reflections as possible and data sets of the higher temperatures were collected with neutrons of wavelength 0·844 Å in order to get more incoming beam intensity and subsequently better statistics of the diffracted intensities as the temperature factor for lead decreases rapidly with temperature.

The monochromatic beam was obtained by reflection from a Cu crystal in transmission geometry. For the 0.535 Å neutrons a Hf filter and for the 0·844 Å neutrons an Er filter placed in the incoming beam reduced the second-order contamination to less than 0·25%. Coupled ω–2θ step scans were used to record the reflection profiles in the bisecting geometry and the number of steps in each profile was 41. The step length was varied as a function of the Bragg angle so that approximately half the points were recordings of background. The observed full widths of reflections may be approximated by the following expressions (in radians): $0{\cdot}017 + 0{\cdot}039 \tan\theta$ for 0·535 Å data and $0{\cdot}035 + 0{\cdot}017 \tan\theta$ for 0·844 Å. The aperture of the detector had a circular opening of 16 mm diameter with sample-to-detector distance of 530 mm. The observed intensity is the average of integrations of the reflection profile measured at three or four symmetry-related positions. The internal agreement among intensities in all cases was close to 2%.

The full data sets were collected for both wavelengths at 293 and 473 K. The data sets were purposely collected in a somewhat random order with respect to temperature to help rule out time correlation from observed temperature correlations in parameters. In chronological order the six sets of data at wavelength 0·535 Å were collected at ambient temperature, 293 K, and at 100, 140, 210 and 120 K with the crystal cooled in a cryostat and at 473 K with the crystal heated by a stream of hot air. The six sets of data at wavelength 0·844 Å were collected in the order 473, 523, 573, 373 and 593 K at elevated temperatures and finally at ambient temperature, 293 K. The Displex cryostat (Air Products C-1003) used was a closed-loop helium refrigeration system with a temperature controller based on a KP/Au–0·07 Fe thermocouple calibrated to the phase-transition temperature, 122·4 K, of a KDP single crystal. The heating equipment (Argoud, Capponi, Chenavas, Marezio & Pontonnier, 1977) sends a stream of hot air coaxially with the neutron beam onto the crystal. An estimate of the stability of the gas temperature at the sample position was obtained in a study on quartz (Wright & Lehmann, 1981) and showed that the temperature variations for a set temperature were less than a degree over a period of several days.

Integrated intensities were evaluated by the $\sigma(I)/I$ criteria (Lehmann & Larsen, 1974), which divides the step-scanned profile into peak and background in such a way that $\sigma(I)/I$ is minimized. Here I is the integrated intensity and $\sigma(I)$ is its e.s.d. based on counting statistics. The contribution from one-phonon acoustic modes to the thermal diffuse scattering (TDS) peaks under the Bragg peaks. Lead is a very soft material and as the data sets extend to quite high values of $\sin\theta/\lambda$ and to high temperatures (the 593 K data has maximum value $\sin\theta/\lambda = 0{\cdot}894$ Å^{-1}) there is an appreciable contribution of TDS especially in the high-order intensities. The expression for the TDS contribution to the integrated intensities to a first approximation has the form of a temperature factor (Cooper, 1970). Reliable correction for TDS is therefore crucial for the determination of accurate parameters describing the atomic vibrations. Neglect of TDS will result in too small values for the mean-square amplitudes of vibration.

Both the 0·535 Å (7394 m s^{-1}) and the 0·844 Å (4687 m s^{-1}) neutrons are much faster than the maximum (~600 m s^{-1}) velocity of acoustic phonons in lead, and the correction for TDS can be approximated very well with the standard X-ray correction. Anisotropic one-phonon TDS corrections were calculated using the computer program *SXTDS*1 (Merisalo & Kurittu, 1978).

Elastic constants at different temperatures were evaluated according to Varshni (1970). In order to illustrate the anisotropy and the dependence on scattering angle and temperature, TDS correction factors α for some of the data sets have been plotted as a function of $\sin\theta/\lambda$ in Fig. 1. At higher temperatures there is a marked anisotropy especially for high-angle reflections which are crucial in the determination of thermal parameters. Refinement is generally improved after the TDS correction.

Wilson plots were calculated to get an overview of the data corrected for TDS. Fig. 2 shows that all data points of the 100, 293 and 473 K sets, even those of the strongest low-order reflections, lie closely on the straight lines, which indicates that this lead sample gives very little extinction.

Results and discussion

Experimental values of the OPP parameters were determined separately at each temperature by the method of least-squares. The quantity minimized in the refinements was

$$M = \sum w(F_o^2 - k^2 y F_c^2)^2;\; w = 1/[\sigma(\text{counting}) + pF_o^2]^2,$$

where k is the scale factor, y is the extinction factor taken in the Zachariasen approximation (Coppens & Hamilton, 1970), and the summation is taken over all sets of observed and calculated structure factors, F_o and F_c, respectively. Minimization was effected by the Fortran subroutine described by Silin & Kobine (1971). In an analysis of weights a value of $p = 0{\cdot}01$ was found to give the flattest distribution of $\langle w(F_o^2 - k^2F_c^2)^2\rangle$ as a function of both $\sin\theta$ and F_o. Extinction is very moderate. Even at the lowest temperatures the strongest reflection had a value of the extinction factor not smaller than 0·98 and values only a thousandth from unity for high-angle reflections which are crucial in the determination of the OPP parameters. For illustration of the correlation effects, the least-squares correlation matrix for the final refinement of the 523 K data is given in Table 1. The correlation is largest between the harmonic parameter α and the isotropic anharmonic parameter γ, an anticipated result, but no correlation is too large to render the least-squares matrix inconvertible.

The results of the refinements carried out with the harmonic and anharmonic model are listed in Table 2. Significance tests (Hamilton, 1965) show that the improvement of the agreement factors resulting from

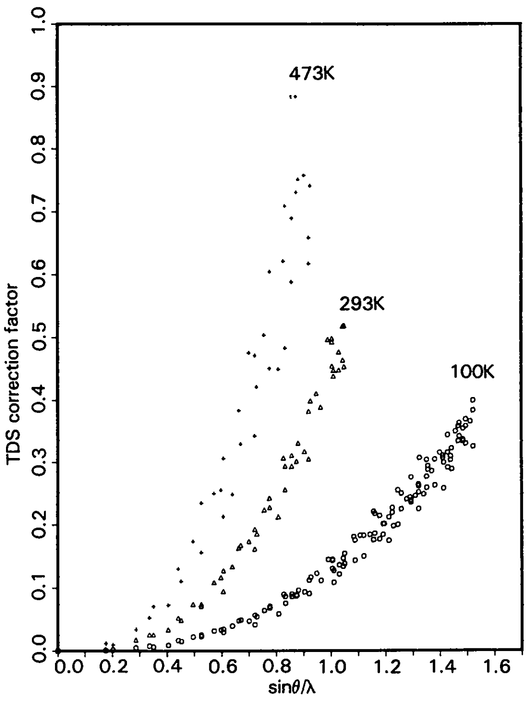

Fig. 1. TDS correction factors (the ratio of TDS intensity to Bragg intensity) for the 100, 293 and 473 K data sets for Pb as a function of $\sin\theta/\lambda$.

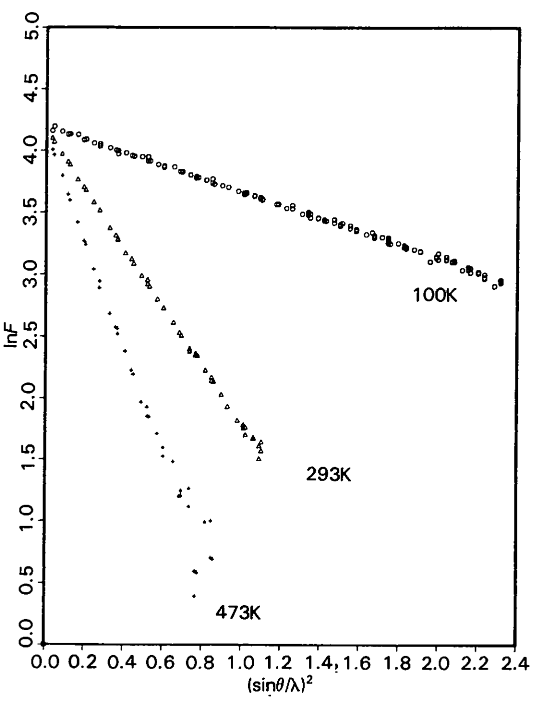

Fig. 2. Wilson (1942) plots for the 100, 293 and 473 K data sets for Pb using 0·535 Å neutrons.

Table 1. *Least-squares correlation matrix for the refinement of the* 523 K *data for* Pb

α, γ and δ are the coefficients of the potential expansion (2), g' is the extinction parameter (Coppens & Hamilton, 1970) and k is the scale factor.

	α	γ	δ	g'	k
α	1·000				
γ	0·975	1·000			
δ	0·381	0·259	1·000		
g'	0·479	0·628	0·046	1·000	
k	0·575	0·732	0·060	0·933	1·000

inclusion of the anharmonic parameters is indeed significant, generally at a level higher than 99·5%. The effect of large correlations on the results is manifested in the values of the standard deviations of the parameters. For example, the large α–γ correlation has an effect of bringing on high values of the standard deviation of γ and making those of α far worse than in the harmonic refinement (*cf.* Table 2).

The observed values of the harmonic force constant α as a function of temperature are illustrated in Fig. 3. Clearly, there is a systematic decrease of the α values with increasing temperature and a temperature-independent OPP model is inadequate. According to the quasiharmonic approximation, temperature variation of the Einstein frequencies ω_E depends on the relative volume change, $\Delta\omega_E/\omega_E = -\gamma_G \Delta V/V$, and consequently the temperature variation of the harmonic parameter α can be written

$$\alpha(T) = \alpha(T_0)[1 - 2\gamma_G \chi(T - T_0)], \qquad (5)$$

where γ_G is the Grüneisen constant, $\chi(T)$ is the volume coefficient of thermal expansion and T_0 is a particular reference temperature. The use of the thermal expansion data given by Cordoba & Brooks (1972), the value $\gamma_G = 2{\cdot}7$ (Leadbetter, 1968), and various reference temperatures then yields the quasiharmonic temperature dependence represented by solid lines in Fig. 3. It is quite obvious that the observed temperature dependence of α is of the Grüneisen type only above $T \gtrsim 350$ K, while the use

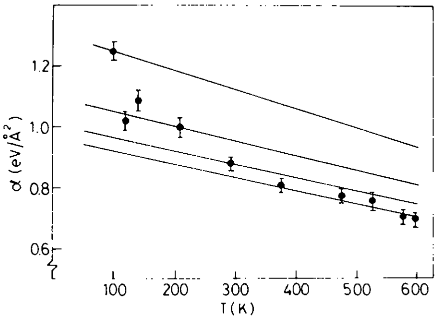

Fig. 3. Observed values of the harmonic parameter α for Pb as a function of temperature. Solid lines represent quasiharmonic temperature dependence calculated from equation (5) with four reference temperatures $T_0 = 100$, 210, 293 and 373 K and the value 2·7 for the Grüneisen parameter.

Table 2. *Results of refinements of neutron diffraction data for* Pb *in the framework of the OPP model*

T is the absolute temperature and N is the number of reflections not related by symmetry. The harmonic parameter α is given in units of eV Å^{-2} and the anharmonic parameters γ and δ in units of eV Å^{-4}. The Einstein angular frequency ω is related to α by $\omega = (\alpha/m)^{1/2}$ and is given in units of 10^{12} s^{-1}. $\langle u^2\rangle$ is the mean-square displacement defined by equation (4) and given in units of Å^2. The weighted R factor is defined by $wR(F^2) = (\sum w|F^2_{\rm obs} - F^2_{\rm calc}|^2/\sum wF^4_{\rm obs})^{1/2}$. The figures in parentheses are e.s.d.'s. Refinements indicated by an asterisk are on data sets collected with the longer wavelength ($\lambda = 0{\cdot}844$ Å). The goodness-of-fit parameter, S, is defined by $S = [\sum w(F^2_{\rm obs} - F^2_{\rm calc})^2/(N-n)]^{1/2}$, where n is the number of variables.

T	N	α	γ	δ	$\langle u^2\rangle$	$wR(F^2)$	ω	S
100	125	1·25 (3)	0·6 (3)	−1·3 (3)	0·0072 (2)	2·15	7·63	1·10
		1·33 (1)	—	—	0·0065 (1)	2·30		
120	45	1·02 (3)	0·8 (2)	−0·4 (2)	0·0088 (3)	3·17	6·89	1·19
		1·12 (1)	—	—	0·0092 (1)	3·54		
140	125	1·09 (3)	−0·3 (1)	−0·5 (1)	0·0128 (4)	2·48	7·12	1·03
		1·06 (1)	—	—	0·0114 (2)	2·80		
210	99	1·00 (3)	−0·3 (1)	−0·21 (6)	0·0215 (6)	3·44	6·82	1·29
		0·94 (1)	—	—	0·0192 (2)	4·19		
293	46	0·87 (2)	−0·10 (6)	≃0	0·0315 (10)	1·88	6·36	1·03
		0·94 (1)	—	—	0·0268 (6)	3·89		
	52*	0·90 (2)	−0·16 (3)	−0·11 (2)	0·0329 (10)	1·71	6·47	1·10
		0·86 (1)	—	—	0·0293 (6)	3·20		
373	35*	0·81 (2)	−0·09 (2)	−0·06 (1)	0·0454 (13)	1·90	6·14	1·29
		0·78 (1)	—	—	0·0411 (7)	2·75		
473	30	0·80 (2)	−0·13 (2)	−0·08 (2)	0·0642 (20)	1·88	6·10	0·99
		0·73 (1)	—	—	0·0558 (12)	3·83		
	31*	0·76 (2)	−0·09 (2)	−0·05 (1)	0·0643 (20)	1·75	5·95	1·09
		0·72 (1)	—	—	0·0568 (12)	3·58		
523	33*	0·76 (3)	−0·10 (3)	≃0	0·0673 (25)	4·15	5·95	1·95
		0·69 (1)	—	—	0·0656 (14)	4·82		
573	35*	0·71 (2)	−0·07 (2)	−0·03 (1)	0·0827 (25)	2·44	5·75	1·26
		0·67 (1)	—	—	0·0739 (15)	4·19		
593	24*	0·70 (3)	−0·06 (2)	−0·02 (1)	0·0846 (35)	2·10	5·71	1·29
		0·67 (1)	—	—	0·0765 (20)	3·38		

of low-temperature reference values ($T \lesssim 350$ K) of $\alpha(T_0)$ cannot explain the observations. Indeed, we conclude that a single OPP is adequate for the description of the temperature dependence of the atomic temperature factor only above $T \gtrsim 4\theta_D$, where the Debye temperature $\theta_D \simeq 90$ K. This observation is incompatible with the experimental results for Be (Larsen, Brown, Lehmann & Merisalo, 1982) as well as with the theoretical considerations for cubic structures (Dawson, 1975; Mair & Wilkins, 1976) for which a single 'quantum' OPP model was estimated to be sufficient to describe the temperature dependence of the harmonic parameter(s) down to about $\theta_D/4$.

The relative frequency shift from the temperature T_1 to T_2 can be defined as $1-\omega(T_2)/\omega(T_1)$. The present results in the validity range of the anharmonic OPP (*i.e.* above 350 K) show approximately linear decreases of frequencies with temperature, and the value of 0·07 is obtained for the relative frequency shift from 300 to 573 K. This value is in close agreement with the value 0·08 calculated in the long-wavelength approximation from the temperature dependence of elastic constants (Varshni, 1970) by averaging over the wavevectors in three principal directions.

The temperature variation of the anharmonic OPP parameters γ and δ is illustrated in Figs. 4 and 5. A common feature with the temperature variation of the harmonic parameters α is that above $T \simeq 4\theta_D$ the anharmonic parameters also obtain values which are approximately constant, or may have possibly a Grüneisen-type temperature dependence. In other words, with regard to the anharmonic terms also the validity range of a single OPP model for Pb seems to be above $T \gtrsim 4\theta_D$.

The lower-temperature ($T < 4\theta_D \simeq 350$ K) behaviour of δ resembles that observed for α in that the increase of the absolute value of δ with decreasing temperature is much more drastic than can be expected from Grüneisen-type softening of the OPP. An analogous effect has been found for Be (Larsen *et al.*, 1982).

The variation of the observed values of γ at low temperatures is more complex. Starting from a virtually constant negative value at high temperatures the γ values decrease with decreasing temperature evidently reaching a minimum around 200 K. With further decrease of temperature the γ-values become positive, at about 100 K. This result implies softening of the OPP at higher temperatures and hardening at lower temperatures and, moreover, there may even exist a critical temperature where the anharmonic isotropic interactions cancel each other or sum up to zero.

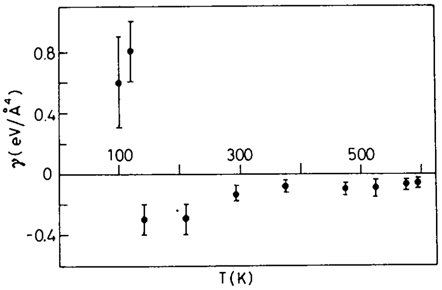

Fig. 4. Observed values of the anharmonic parameter γ for Pb as a function of temperature.

In order to check the influence of the anisotropic TDS correction on the results the refinements were also carried out on the data not corrected for TDS. The general behaviour of the values of the potential parameters with temperature was found to be practically identical to that shown in Figs. 3–5, indicating that the results given above are not consequences of possible shortcomings in the TDS correction.

It is interesting to note that both the expansion coefficient (Rubin, Johnston & Altman, 1962) and the specific heat capacity (Meads, Forsythe & Giauque, 1941) also show irregular behaviour around 100 K.

The observations stated above deserve a few comments. It is conventionally anticipated that the Debye temperature of a material is an approximate temperature limit above which the Boltzmann distribution function with a single OPP is an adequate model for the thermal smearing function (the probability density function) of an atom. Adequacy of a model is judged here by its ability to predict succesfully the observations over the entire temperature range $T > \theta_D$ with the OPP having only a Grüneisen-type temperature dependence of force constants. Indeed, this anticipation has been proved correct by a number of X-ray and neutron diffraction experiments. The use of a quantum statistical OPP formalism has been shown to extend the validity of this model even down to $\theta_D/3-\theta_D/4$ (Larsen *et al.*, 1982). The present experimental results show that for Pb the validity limit of the OPP model is far higher, at about $4\theta_D$. Further analysis also showed that this limit is independent of the statistics used, either classical or

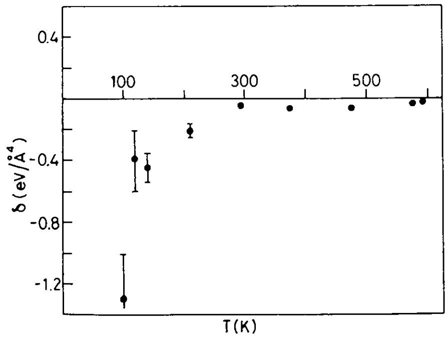

Fig. 5. Observed values of the anharmonic parameter δ for Pb as a function of temperature. When not otherwise indicated error bars lie within heavy dots.

quantum. Consequently, precautions should be excercised. The validity range of the OPP model should be verified by measuring full data sets at various temperatures over the whole temperature range, from very low temperatures to near the melting point, instead of studying temperature variation of one or two reflections. So far, this sort of measurement has been carried out in only a few cases (see, for example, Moss, McMullan & Koetzle, 1980; Larsen *et al.*, 1982).

Obviously, the failure of the OPP model for Pb at fairly high temperatures is a manifestation of the quite complex interatomic forces. This surmise is borne out by the experimental dispersion relations which contain so many irregularities that they cannot be accounted for by any relatively simple model of interatomic forces (Stedman, Almqvist, Nilsson & Raunio, 1967). Brockhouse, Arese, Caglioti, Rao & Woods (1962) suggested that interactions out to seventeenth neighbours might be necessary to reproduce their results and sometimes are of alternating sign. A theoretical study of Born–von Karman fit by Cowley (1974) shows that interactions out to eight neighbours exist in Pb. Consequently, the inadequacy of a model of independent vibrations is readily perceivable.

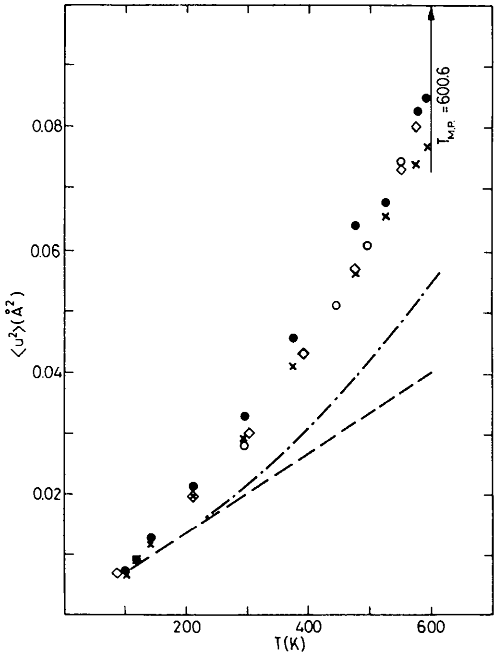

Fig. 6. Mean-square displacements for Pb as a function of temperature. Present experimental values refined in the harmonic model (×) are in close agreement with neutron powder diffraction results (○) of Lisher (1976) and values determined from Chipman's (1960) X-ray data (◇). Present experimental values obtained from final refinements in the framework of the anharmonic model (●) indicate the softening effect of anharmonic interactions in Pb. Temperature dependence predicted by the harmonic approximation (– – – –), equation (4) with $\gamma = 0$, and the quasiharmonic approximation (– · – · –), equation (5) with $\alpha = k_BT/\langle u^2\rangle$, with 100 K values as references are clearly inadequate. The results of Zarochentsev *et al.* (1976) are not presented because no numerical values were given.

Fig. 6 exhibits a comparison of the present results with the earlier diffraction studies in terms of the mean-square displacement. Where the present data are fitted to the harmonic model there is a close agreement with the earlier results except at the very highest temperatures close to the melting point. Bearing in mind that the three studies were carried out applying different techniques, we conclude that the data are not contaminated by serious experimental errors and, furthermore, that the TDS corrections, which were calculated in different ways for the different sets of measurements, are consistent. The mean-square displacements calculated for the anharmonic model are systematically above those calculated for the harmonic model and demonstrate the softening effect of the anharmonic interactions in Pb. Extrapolation curves for harmonic and quasiharmonic models exhibit inadequacy of these models.

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Site-Symmetry Restrictions on Thermal-Motion-Tensor Coefficients up to Rank 8

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Abstract

An extension of the tables for the site-symmetry restrictions on the thermal-motion-tensor coefficients to include tensors up to rank 6 (up to rank 8 for cubic, hexagonal, tetragonal and trigonal site symmetries) is presented. The dependence relationships of these symmetric polar tensors are calculated in their natural crystallographic lattice frames using a direct method.

Introduction

Recently there has been a growing interest in the study of anharmonicity in thermal motion; anharmonic parameters are essential, for example, in modelling the structures of fast ionic conductors or other disordered systems like ferroelectrics. These highly anharmonic systems very often need thermal parameters higher than fourth order to obtain a satisfactory description. Moreover, anisotropic modifications in a plane of hexagonal symmetry can be described only with sixth- (or higher) order terms. Nowadays the accuracy and precision of diffraction data are in general no longer an obstacle to a meaningful refinement of such high-order thermal parameters in a least-squares procedure, *e.g.* $CsPbCl_3$ (Hutton & Nelmes, 1981), Li_3N (Zucker & Schulz, 1982), Ag_3SI (Perenthaler & Schulz, 1981), PbF_2 (Schulz, Perenthaler & Zucker, 1982), $RbAg_4I_5$ (Kuhs, 1983). Crystallographic program systems like *PROMETHEUS* (Zucker, Perenthaler, Kuhs, Bachmann & Schulz, 1983) allow for the routine insertion and refinement of parameters up to sixth order. To facilitate a general application, a tabulation of the symmetry constraints for all crystallographic site symmetries is clearly needed.

Whilst the symmetry restrictions of, for example, the elastic coefficients based on orthogonal lattice frames are at least partially available up to twelfth order (*i.e.* sixth-order elastic constants) (Chung & Li, 1974; Brendel, 1979; Fumi & Ripamonti, 1983), a tabulation for general (even- and odd-rank) symmetric polar tensors based on the natural crystallographic lattice frames is available only for tensors up to fourth order (Johnson & Levy, 1974). This paper presents the extension of that tabulation.

Method

The method used to derive the dependence relations for symmetric polar tensor coefficients is based on the fundamental transformation law for tensors ('direct method'). A tensor coefficient remains unchanged when the transformation corresponds to the site symmetry:

$$C_T^{jklmnp\ldots} = T_{jq}T_{kr}T_{ls}T_{mt}T_{nu}T_{pv}\ldots C^{qrstuv\ldots}$$

with $C_T^{jklmnp\ldots} = C^{qrstuv\ldots}$ and $1 \leq j, k, l, m, n, p, q, r, s, t, u, v \ldots \leq 3$. The point-group generators **T** were taken from Johnson & Levy (1974). For site symmetries having several generators all of them have been treated simultaneously. The homogeneous system of equations obtained (one equation for each coefficient) was reduced using a Gaussian elimination procedure. The order of assignment of independency is with increasing indices of the coefficients, except for the unmixed coefficients C^{jjjjjj}, which have highest priority in every case.* The correctness of the remaining system of equations giving the dependence relationships was checked algebraically by inserting numerical values. In addition, the number of unrestricted parameters was checked by comparison with results obtained by group-theoretical calculations (Sirotin, 1960).

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* This is the same ordering, as, for example, in the *PROMETHEUS* system (Zucker, Perenthaler, Kuhs, Bachmann & Schulz, 1983).

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