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An X-ray Diffraction Study of Potassium

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Abstract

Accurate relative and absolute integrated intensities have been measured in an X-ray diffraction experiment on two single crystals of potassium in the temperature range 207 to 337 K. In order to examine the possible significance of anharmonic contributions to the atomic vibrations and the temperature factor, the data were analysed with a fourth-order anharmonic one-particle potential of the form $V(u) = \frac{1}{2}\alpha u^2 + \gamma u^4 + \delta(u_x^4 + u_y^4 + u_z^4 - \frac{3}{5}u^4)$. The isotropic parameter γ and the anisotropic parameter δ were both found to be significant, with respective values averaged from the data from the two crystals of -45 ± 5 eV nm^{-4} and $+41 \pm 5$ eV nm^{-4}. The positive sign of δ indicates that there is a greater probability of vibration of the atoms in the nearest-neighbour directions than the next-nearest-neighbour directions. A possible explanation for this in terms of rapid migration of lattice vacancies is suggested. The average value of the harmonic parameter α at 293 K was $15{\cdot}1 \pm 0{\cdot}3$ eV nm^{-2}, from which the root-mean-square vibration amplitude was determined as $u_{\rm r.m.s.} = 0{\cdot}0741 \pm 0{\cdot}0012$ nm at 293 K, and the Debye temperature was determined as 81 ± 1 K.

Introduction

In recent years there has been considerable interest in the anharmonic lattice dynamics of simple structures, in particular, the elements. One experimental approach to the subject of anharmonicity is the study of the Debye–Waller factor by elastic X-ray or neutron scattering, from which the harmonic and anharmonic components of the probability distribution function of atomic displacements may be deduced.

Perhaps the most fundamental of metal crystals are alkali metals characterized by an inert gas core and a nearly free conduction electron. An X-ray diffraction study of anharmonicity in sodium has already been prepared in two papers by Field & Medlin (1974) and Field & Bednarz (1976). This paper details a further study of this type on potassium, and a similar study on lithium (Bednarz & Field, 1982) is published later in this issue.

Theory

The generalized structure-factor formalism of Dawson (1967) has proved a useful basis for the interpretation of diffraction data.

Potassium crystallizes in a body-centred cubic structure with a space group of *Im*3*m*. The two atoms per unit cell are each at a centre of point symmetry *m*3*m*. In this case the structure factor F in Dawson's formalism reduces to

$$F = 2f_c\,\tau_c,$$

where f_c is a centrosymmetric scattering factor and τ_c is a centrosymmetric temperature factor. No antisymmetric terms arise in the structure factor because the atoms are at centres of symmetry, hence there is no possibility of observing 'quasi-forbidden' reflections as have been reported recently for several elements of lower symmetry, such as tetragonal white tin (Merisalo & Järvinen, 1978) or hexagonal zinc (Merisalo, Järvinen & Kurittu, 1978) and cadmium (Merisalo, Peljo & Soininen, 1978).

If it is supposed that the electron distribution and probability distribution function for the atoms are distorted from spherical by the crystal field, the structure factor may be rewritten as

$$F = 2(\bar{f}_c\,\bar{\tau}_c + \bar{f}_c\,\delta\tau_c + \bar{\tau}_c\,\delta f_c), \qquad (1)$$

where $\bar{f}_c$ and $\bar{\tau}_c$ represent spherically symmetric quantities, and δf_c and $\delta\tau_c$ represent anisotropic but centrosymmetric contributions to the scattering and temperature factors respectively by the crystal field.

Potassium is almost an ideal free-electron metal. The number of free charge carriers per atom has been determined from the Hall coefficient as 0·99 by Goodman (1968), and the Fermi surface has been found by Dagens & Perrot (1973) to be distorted by less than 0·2% in any direction from the free-electron surface. Further, the contribution of the free electron to the structure factor even at the first reciprocal-lattice

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point is unobservable. Therefore, any contribution to δf_c in (1) must be due to distortion of the core-electron rather than of the valence-electron distribution.

Now, potassium is soft, with small elastic constants, has a low melting point of 336·8 K, and has large atomic vibration amplitudes. This suggests the strong possibility of anharmonic effects giving rise to a $\delta\tau_c$ term in (1). Thus, although in principle the contributions to the structure factor due to solid-state effects on wave functions and anharmonic effects are inseparable in an X-ray diffraction experiment, the assumption that the latter is much more probable is justified, and the term in δf_c in (1) may be neglected.

It is assumed that the anharmonic effects for a potassium crystal may be described in terms of a one-particle potential. The appropriate form to fourth order for atoms at *m*3*m* symmetry points as in potassium is given by

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

where

$$u^2 = u_x^2 + u_y^2 + u_z^2$$

and u_x, u_y, u_z represent components of the atomic displacement $\mathbf{u}$. Following Willis (1969), this yields a temperature factor of

$$\begin{aligned}\tau_c = N \exp[-2\pi^2(h^2+k^2+l^2)\,k_B T/\alpha a^2] \\ \times \Bigg\{1 - 15k_B T\frac{\gamma}{\alpha^2} + 10(k_B T)^2\left(\frac{2\pi}{a}\right)^2\left(\frac{\gamma}{\alpha^3}\right) \\ \times (h^2+k^2+l^2) - (k_B T)^3\left(\frac{2\pi}{a}\right)^4\left(\frac{\gamma}{\alpha^4}\right) \\ \times (h^2+k^2+l^2)^2 - (k_B T)^3\left(\frac{2\pi}{a}\right)^4\left(\frac{\delta}{\alpha^4}\right) \\ \times [h^4+k^4+l^4 - \tfrac{3}{5}(h^2+k^2+l^2)^2]\Bigg\}, \qquad (2)\end{aligned}$$

where

$$N = \left[1 - 15k_B T\left(\frac{\gamma}{\alpha^2}\right)\right]^{-1}.$$

Here h, k, l are the Miller indices, k_B is Boltzmann's constant, T is the temperature and a is the lattice constant.

In the harmonic approximation (γ, $\delta = 0$),

$$u_{\text{r.m.s.}} = \langle u^2\rangle^{1/2} = \left[\frac{3k_B T}{\alpha}\right]^{1/2}, \qquad (3)$$

where $u_{\text{r.m.s.}}$ is the root-mean-square vibration amplitude.

It can also be shown that

$$\langle u^4\rangle = N\left[15\left(\frac{k_B T}{\alpha}\right)^2 - 945\left(\frac{\gamma}{\alpha^4}\right)(k_B T)^3\right].$$

In the harmonic case, the ratio

$$r = \langle u^4\rangle/\langle u^2\rangle^2$$

gives $r = \tfrac{5}{3}$, and deviations from this figure show the extent of the contribution of the anharmonic term γ to the vibration amplitudes.

Experimental

The potassium metal used was of 99·97% purity and was supplied by Koch Light Laboratories. Single crystals were grown in commercial glass capillaries of ~0·01 mm wall thickness and negligible absorption and background scattering for Mo $K\alpha$ radiation. The capillaries were sealed at either end in a flame after the potassium specimens were inserted. The crystals were less than 0·5 mm in diameter to conform to the requirement that the entire crystal be bathed in the X-ray beam.

Two crystals were prepared. The first was cylindrical in shape and protected from contamination in the capillary tube by petroleum jelly. The second was spherical and was prepared in an argon atmosphere. In order to prevent oxidation, a further piece of potassium was pushed into the end of the capillary before sealing in the flame. The crystals were grown by slow cooling from the melt in a bath of petroleum jelly.

Integrated intensities of the reflections were measured on a STOE on-line automatic two-circle diffractometer operating in Weissenberg mode. Mo $K\alpha$ radiation was used, and a graphite-crystal monochromator was used in the incident beam.

Intensities were collected in the temperature range 207–308 K on crystal 1, and 297–337 K on crystal 2. The low-temperature measurements were made with a STOE low-temperature attachment in which the crystal was cooled by an air stream which had been passed through heat-exchanging coils in a Dewar of liquid nitrogen. The temperature was monitored by a chromel–alumel thermocouple tip about 5 mm from the crystal. The airstream was diffused by a small disc to provide a uniform temperature distribution in the vicinity of the crystal. Gas flow was controlled by an on–off valve switched from the thermocouple output, a large pressurized container to act as a mechanical buffer against surges in gas flow, and by needle valves. The precision of the temperature control was 1 K. The low-temperature limit of the experiment was set by the fact that the crystal showed signs of thermal shock when cooled below 200 K.

The measurements above room temperature were made with the crystal still mounted on the low-temperature stage on the diffractometer. However, no air stream was passed over the crystal, which was heated by radiant heat from a 150 W lamp. Temperature stability in this case was ±0·5 K.

Intensities for higher-angle reflections were weak because the large thermal vibration amplitude produces a rapid fall off in intensity with Bragg angle. The scanning method used was the $\omega/2\omega$ mode. It was observed experimentally that background was significantly reduced for this scan mode as compared with an ω scan for the same volume swept out in reciprocal space. Since a major component of this background was thermal diffuse scattering (TDS), the TDS correction was also reduced. This was confirmed by calculation of the TDS for both scan modes. Equal times were spent on measuring integrated intensity and background for each reflection in order to ensure good counting statistics.

Both crystals were aligned along a $\langle 110\rangle$ axis. This has the advantage that pairs of independent reflections occurring at the same Bragg angle, such as 330 and 411, or 431 and $5\bar{1}0$, occur on the same layer. These pairs are important because differences in intensities between individual members of such pairs of reflections are indicative of anisotropic anharmonic effects. However, for equi-inclination geometry and a $\langle 110\rangle$ rotation axis, all data collected on any non-zero even layer are necessarily collected under conditions of multiple diffraction, in addition to the possibility of 'accidental' multiple diffraction. The intensities of symmetry-related reflections on different layers were checked and found to be self-consistent and it was concluded that multiple diffraction was having no effect on the data.

In the data analysis, the intensities measured from each crystal were scaled to model-calculated intensities. However, the absolute scale factor was determined experimentally for the second (spherical) crystal by measuring the incident-beam intensity. The incident-beam cross-sectional distribution was measured with a pinhole in gold foil of nominal thickness 125 μm. The diameter of the pinhole was measured on a travelling microscope and was found to be 72·7 ± 0·5 μm. The intensity distribution across the area taken up by the crystal in the beam was uniform to 2% in the vertical direction, but was not uniform in the horizontal direction. An average incident intensity was calculated by integrating over all the pinhole measurements in the beam cross section. The value determined for the absolute scale factor was

$$k_s = 5960 \pm 470.$$

Data

After crystal 1 was cooled, it was found that there was a time dependence of the intensities of some lower-angle reflections at room temperature, as the crystal annealed. The reflections concerned were therefore subject to variable extinction for which no correction could be made. These reflections were of the types 110, 200, 211, 220 and 310, and they were discarded from the analysis. This phenomenon is consistent with a similar annealing in sodium reported by Field & Bednarz (1976).

The data collected from crystal 1 were as follows. The temperature dependence of the intensity of one reflection for each of the types 222, 400, 330 and 411 was observed in the temperature range 207 to 313 K. 80 integrated intensities were obtained. In addition, the intensities of all symmetry-related reflections on the zero and first layers of a $\langle 110\rangle$ zone were collected at 308, 296 and 233 K. Excluding extinction-affected reflections, this contributed 47 data points which are the means of the intensities of equivalent reflections at the same temperature.

The data collected on crystal 2 were as follows. The intensities of all symmetry-related reflections on the zero and first layers, and the 420 reflections on the second layer of a $\langle 110\rangle$ zone were measured from room temperature to the melting point. Excluding extinction-affected reflections, 108 data points, each of which was the mean of equivalent reflections collected, were retained for analysis.

Data analysis

Correction factors were applied carefully in order to ensure as great an accuracy as possible in the results. In making the Lorentz–polarization correction, the polarization ratio was taken as the mean of the perfect and ideally imperfect monochromator crystal values, although there is only about 2% difference between these values for a graphite crystal in Mo $K\alpha$ radiation. Anomalous dispersion corrections were made with values of the corrections f' and f'' taken from *International Tables for X-ray Crystallography* (1974). Absorption corrections were calculated numerically.

Thermal diffuse scattering (TDS) is large in a crystal like potassium having large vibration amplitudes. In addition, potassium is highly elastically anisotropic. First-order TDS corrections were made based on a modification of the method of Rouse & Cooper (1969) which takes into account the anisotropy of the TDS. The modification made was to extend the Rouse & Cooper formalism from zero-layer to upper-level equi-inclination geometry. The elastic constants used in the correction program were taken from Marquardt & Trivisonno (1965) and Smith & Smith (1965).

The data were analysed by minimizing the quantity

$$\chi^2 = \sum_i \omega_i (I_{oi} - I_{ci})^2,$$

where I_{oi} represents the ith corrected observed intensity with a weighting factor ω_i given by

$$\omega_i = \frac{1}{\sigma_i^2},$$

where σ_i was the estimated error in I_{oi}. I_{ci} represents the ith calculated intensity given by

$$I_{ci}=k_s\bar{f}_{ci}^2\,\tau_{ci}^2,$$

where the τ_{ci} were determined from (2), and the scattering factors $\bar{f}_{ci}$ were generated from the nine-parameter-fit tables of Doyle & Turner (1968). The value of the lattice parameter adopted for the present work was 0·5329 nm calculated from the measured density of potassium as given by Stokes (1966) and Schouten & Swensen (1974). The variation with temperature of the unit-cell lattice parameter a was explicitly accounted for in evaluating $\bar{f}_c$ and τ_c. The relative scale factor was given by

$$k_s=\frac{\sum\limits_i \omega_i I_{oi}\bar{f}_{ci}^2\,\tau_{ci}^2}{\sum\limits_i \omega_i \bar{f}_{ci}^4\,\tau_{ci}^4},$$

which satisfies the condition $\partial\chi^2/\partial k_s=0$.

The temperature dependence of the potential parameter α was taken into account by the quasi-harmonic expression

$$\alpha=\alpha_0(1-2\gamma_G\,\chi_v\,T), \qquad (4)$$

where values of the Gruneisen constant γ_G and the volume coefficient of expansion χ_v were taken from the literature. It has been assumed by various authors, for example Willis (1969), that the parameters γ and δ also vary according to a quasi-harmonic expression similar to that in (4). However, it was found in the data analysis that the errors in refined values of γ and δ were rather larger than the predicted quasi-harmonic variation, so no correction for the temperature dependence of γ and δ was made.

Four models were used in the data analysis. In model 1, χ^2 was minimized with potential parameter γ zero. The parameters refined were then α_0, δ and k_s. In model 2, the parameter γ was allowed to vary. Now Dawson (1975) has pointed out that the γ term may be simulated by choosing values of γ_G larger than measured values. The extent to which this was possible was investigated in model 3, in which γ was taken as zero and γ_G allowed to vary, and in model 4, in which γ_G was taken as the value obtained in the refinement of model 3, and γ allowed to vary. A summary of the details of these models is given in Table 1.

Table 1. *Summary of models*

Model	Fixed parameters	Refined parameters
1	$\gamma=0$ γ_G (literature value)	α_0, δ, k_s
2	γ_G (literature value)	α_0, γ, δ, k_s
3	$\gamma=0$	α_0, δ, γ_G, k_s
4	γ_G (value from model 3)	α_0, γ, δ, k_s

The measure of agreement between observed data and theoretical models was given by

$$R=\left|\frac{\sum\limits_i \omega_i(I_{oi}-I_{ci})^2}{\sum\limits_i \omega_i I_{oi}^2}\right|^{1/2}.$$

The tables of Hamilton (1965) were used to assess the significance of the anharmonic terms. These tables were also used to estimate the errors in optimum parameters. For a data set of N points described by m refined parameters, the error Δp_i in parameter p_i was taken as that value which gave the R-factor ratio

$$\frac{R(p_i+\Delta p_i)}{R(p_i)}=\mathscr{R}_{1,N-m,0\cdot25},$$

where $\mathscr{R}$ is a distribution of R factors given by Hamilton. In this case the probability of an R-factor ratio greater than $\mathscr{R}_{1,N-m,0\cdot25}$ is 0·25, and Δp_i corresponds approximately to a standard deviation.

Results

The volume coefficient of expansion χ_v was taken from Kittel (1971) as 249 MK^{-1}.

There are a number of published values of the Gruneisen constant γ_G of potassium covering the range from 1·15 given by Gerlich (1975) through 1·22 given by Schouten & Swensen (1974) to 1·34 given by Slater (1939). Further, the dependence of γ_G on phonon frequency has been studied by various authors such as Srivastava & Singh (1970), Kushwaha & Rajput (1975), Meyer, Dolling, Kalus, Vettier & Paureau (1976) and Taylor & Glyde (1976). Their results imply that the mean value of γ_G in the Brillouin zone is $\sim$1·3. Initially, refinements with models 1 and 2 were made with each of the values of 1·15, 1·22 and 1·34 for γ_G. It was found that the R factor was consistently lower where 1·34 was used, and any results tabulated below for models 1 and 2 refer to the refinement made with $\gamma_G=1{\cdot}34$.

The parameters refined for each of the four models from the data for crystal 1 are given in Table 2, and similarly for crystal 2 in Table 3. In the tables, the R' values are the R factors obtained for refinements with δ set to zero. The parameter α_{293} is the value of α at $T=293$ K.

Values of the observed structure factors F_o were calculated for the data recorded at 296 K from crystal 2 by rescaling to structure factors F_c given by

$$F_c=2\bar{f}_c\,\tau_c,$$

where the τ_c were calculated from the potential parameters listed for model 2 in Table 3 for crystal 2.

Table 2. *Parameters refined from the data of crystal* 1

	Model			
	1	2	3	4
γ_G	1·34	1·34	1·80	1·80
α_0 (eV nm^{-2})	18·7 ± 0·1	19·2 ± 0·1	20·6 ± 0·1	20·6 ± 0·1
γ (eV nm^{-4})	0·0	−39 ± 6	0·0	0 ± 5
δ (eV nm^{-4})	37 ± 10	36 ± 10	38 ± 8	38 ± 8
k_s	9540 ± 300	10290 ± 600	8980 ± 200	8980 ± 500
R (%)	5·96	5·29	4·76	4·76
R' (%)	6·62	5·92	5·52	5·52
α_{293} (eV nm^{-2})	15·0 ± 0·1	15·4 ± 0·1	15·2 ± 0·1	15·2 ± 0·1
$u_{\text{r.m.s.}}$ at 293 K (nm)	0·0710 ± 0·0002	0·0729 ± 0·0006	0·0706 ± 0·0002	0·0706 ± 0·0002
r	1·667	1·704 ± 0·003	1·667	1·667 ± 0·003

Table 3. *Parameters refined from the data of crystal* 2

	Model			
	1	2	3	4
γ_G	1·34	1·34	1·93	1·93
α_0 (eV nm^{-2})	18·6 ± 0·1	18·4 ± 0·1	21·0 ± 0·1	21·0 ± 0·1
γ (eV nm^{-4})	0·0	−51 ± 8	0·0	−22 ± 8
δ (eV nm^{-4})	49 ± 5	45 ± 4	49 ± 4	47 ± 4
k_s	4040 ± 120	5680 ± 500	4050 ± 100	4660 ± 400
R (%)	5·12	4·04	4·08	3·86
R' (%)	9·47	8·93	8·90	8·82
α_{293} (eV nm^{-2})	14·9 ± 0·1	14·8 ± 0·1	15·1 ± 0·1	15·1 ± 0·1
$u_{\text{r.m.s.}}$ at 293 K (nm)	0·0712 ± 0·0002	0·0753 ± 0·0008	0·0708 ± 0·0002	0·0725 ± 0·0011
r	1·667	1·710 ± 0·004	1·667	1·691 ± 0·001

The results of this calculation are shown in Table 4, together with an R factor for that data given by

$$R = \left[\frac{\sum_i \frac{1}{\sigma_i^2}(F_{oi} - F_{ci})^2}{\sum_i \frac{1}{\sigma_i^2} F_{oi}^2} \right]^{1/2},$$

where σ_i is the error associated with the ith structure factor.

The complete sets of data for both crystals are listed in Bednarz (1977).

Discussion

(1) *The parameter δ*

The R factor is consistently significantly smaller for all models than the factor R', particularly for the high-temperature data from crystal 2 where the effects of anharmonicity would be expected to be greater than for the low-temperature data of crystal 1. The significance level is better than 0·005. There is almost no correlation between δ and the other parameters refined, and the error in δ is considerably less than the value of δ itself. Therefore there is clearly a significant contribution to the vibrational properties of potassium from the anisotropic anharmonic parameter δ in the one-particle potential.

The positive sign of δ indicates that there is a greater probability of vibration of the atoms in the nearest-neighbour directions, ⟨111⟩, than in the next-nearest-neighbour directions, ⟨100⟩. This is consistent with the result determined for sodium by Field & Bednarz (1976). The observation of the annealing of the crystals

Table 4. *Observed and calculated structure factors at* 296 K *for crystal* 2

Reflection	F_o	F_c	σ
222	2·179	2·211	0·025
321	1·608	1·622	0·007
400	1·171	1·162	0·013
330	0·906	0·912	0·010
411	0·888	0·884	0·010
420	0·683	0·677	0·008
332	0·542	0·541	0·006
422	0·416	0·408	0·005
510	0·293	0·287	0·003
431	0·317	0·316	0·004
521	0·180	0·181	0·002
440	0·162	0·151	0·003
433	0·124	0·125	0·004
530	0·112	0·114	0·007

$R = 1{\cdot}4\%$

at room temperature as indicated by the time dependence of the extinction parameters for the low-angle reflections after cooling suggested that there was considerable motion of vacancies and prompted the following possible explanation of the sign of δ.

It is known from work by Martin (1965) on the heat capacity of potassium that there is a relatively high vacancy concentration of $\sim 10^{-3}$ near the melting point of potassium. Further, the formation of a vacancy is accompanied by a relaxation of neighbouring atoms about the hole in the lattice. Detailed calculations on this process have been carried out by Torrens & Gerl (1969), Rao (1975) and Das, Rao & Vashista (1975). They show that the relaxation is 5 to 7% of the unrelaxed separation of atom and vacancy inward for nearest neighbours and 3 to 4% outward for the next-nearest neighbours. Krivoglaz (1961) has shown that such static displacements are equivalent to a temperature factor. Calculations for potassium showed that static displacements of this magnitude give an anisotropic temperature factor of sign consistent with experiment, but with the anisotropic effect an order of magnitude too small. However, the displacements are not static, because the vacancy migration energy in potassium is only ~0·07 eV (see, for example, Torrens & Gerl), and the vacancies are highly mobile. It is suggested that the large lattice relaxation coupled with a high mobility of lattice vacancies could perturb the one-particle potential to the extent observed and account for the sign and magnitude of δ.

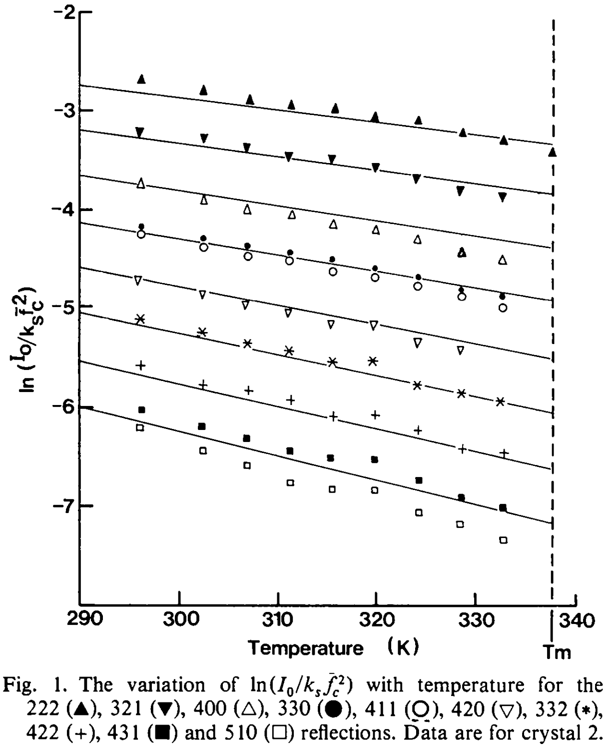

Fig. 1. The variation of $\ln(I_0/k_s f_c^2)$ with temperature for the 222 (▲), 321 (▼), 400 (△), 330 (●), 411 (○), 420 (▽), 332 (*), 422 (+), 431 (■) and 510 (□) reflections. Data are for crystal 2. Tm is the melting point of potassium.

Table 5. *Largest observed differences in intensity between pairs of independent reflections occurring at the same Bragg angle*

Reflections	Temperature (K)	Intensities	Difference (%)
330	333	2433	13
411		2156	
431	333	226	35
510		167	
433	297	90	22
530		74	

In order to illustrate the effect of the anisotropic parameter δ on the intensities, a graph of $\ln(I_0/k_s f_c^2)$ *versus* temperature is shown in Fig. 1. In the harmonic approximation, pairs of independent reflections occurring at the same Bragg angle, like 330 and 411, or 431 and 510, should have identical intensities, but it is evident from the figure that they do not. Indeed, the largest observed differences in intensities between pairs of reflections of this type may be several tens of percent, as shown in Table 5.

The variation of the parameter δ with temperature was calculated for the temperature range from about 230 K to the melting point. This was determined from the intensity ratio of the two pairs of reflections 330, 411 and 431, 510 in that temperature range. The result is plotted in Fig. 2. There is no large increase in δ in this temperature range in contradistinction to the behaviour

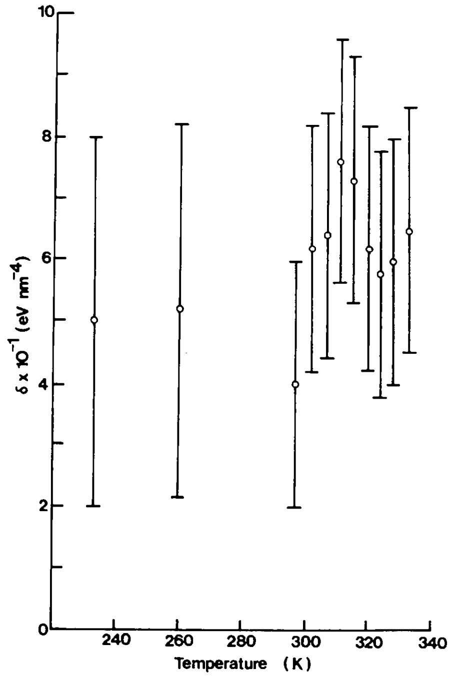

Fig. 2. Observed variation of δ with temperature for potassium.

of δ observed in sodium by Field & Bednarz (1976). However, the trend of the results is that δ does increase with temperature, and not decrease, as would be predicted by a quasi-harmonic expression similar to that given in (4) for α.

(2) *The parameter* γ

It can be seen from Tables 2 and 3 that the R factors for models 3 and 4 where γ_G is allowed to vary are considerably better than those for models 1 and 2 where it is not. This confirms the proposition of Dawson (1975) mentioned earlier. However, given the number of studies on γ_G mentioned earlier, which suggest values of about 1·2 to 1·3, the values for γ_G of 1·8 to 1·9 obtained when it is treated as a refined parameter are unrealistic, and models 3 and 4 may similarly be regarded as unrealistic. The significantly better agreement of model 2 with experiment than model 1, and the small error in γ relative to the value itself in model 2 indicate a genuine significant γ term in the potential. Indeed the value of γ in model 2 is significant at a level of 0·005.

Further confirmatory evidence for the existence of a real γ and against the existence of a large value of γ_G is given by the scale factor for the data from crystal 2. Of the refined values of k_s listed in Table 3, only that for model 2 agrees within experimental error with the measured value of 5960 ± 470. Thus model 2 affords the best description of the data.

The ratio r in model 2 is not much different from the value of 1·667 for the harmonic case. Thus the deviation of the probability distribution function for the atomic displacements from a Gaussian is not large.

(3) *The parameter* α *and quantities derived from it*

The values of α_{293} given in Tables 2 and 3 differ considerably from that obtained from the only other X-ray study on potassium by Krishna Kumar & Viswamitra (1971). The value derived from their experiment is $\alpha_{293} = 20{\cdot}9 \pm 0{\cdot}4$ eV nm^{-2}. However, in our experience, only two of the six reflections examined by Krishna Kumar & Viswamitra could be considered to be reasonably free from extinction, and the high value of α obtained by them probably reflects inadequate extinction estimates in their calculations.

The values of α_{293} given in Tables 2 and 3 are slightly different for the two crystals. It is postulated that this does not necessarily reflect inaccuracies in the experiment. The two sets of data were recorded in different temperature ranges, and since no account was taken of the temperature variation of γ_G and χ_v in the analysis, this may account for the difference in the α_{293} values. For the same reason, the value α_0 is not strictly the actual value of α at 0 K.

The values of $u_{\rm r.m.s.}$ were calculated according to (3). The value for $u_{\rm r.m.s.}$ is large. Indeed, the ratio of the r.m.s. vibration amplitude to the nearest-neighbour separation at the melting point is 17·5 ± 0·4%.

Finally, a harmonic B factor was derived according to

$$B = \frac{8\pi^2}{3}\langle u^2\rangle$$

and an X-ray Debye temperature θ_D was derived according to

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

where M is the atomic mass. The values obtained were

$$B = 0{\cdot}132 \pm 0{\cdot}003\ \text{nm}^2$$

and

$$\theta_D = 81 \pm 1\ \text{K}.$$

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On Anharmonicity in Cadmium

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Abstract

Recent X-ray diffraction data on cadmium [Rossmanith (1978). *Acta Cryst.* A**34**, 497–500] have been reanalysed using a temperature factor based on an anharmonic one-particle potential to fourth order for the atoms, and values for the anharmonic parameters have been obtained. The fourth-order parameters α_{40} and β_{20} are found not to be significantly different from zero, while the other fourth-order parameter γ_{00} is found to be strongly correlated to the extinction correction and harmonic parameters. The third-order antisymmetric parameter is found to have a value of 57 ± 16 eV nm^{-3}, which is in reasonable agreement with a recent measurement. The application of the extinction correction is shown to affect substantially the values for the potential parameters.

Introduction

The determination from X-ray diffraction data of anharmonic parameters in a one-particle-potential model for the atomic vibrations of metals is now well established. It is sometimes possible to evaluate antisymmetric anharmonic components of the potential from measurements of so-called quasi-forbidden reflections. On the other hand, if a complete set of Bragg reflection data at one temperature is available, it is possible in principle to determine all the anharmonic parameters. This has recently been demonstrated in tetragonal tin, where Merisalo & Jarvinen (1978) determined the parameter for the antisymmetric component in the one-particle potential to be $\alpha_{32+} = (390 \pm 30)$ eV nm^{-3} from a measurement on three quasi-forbidden reflections, whereas Field (1978) obtained a value of $\alpha_{32+} = (370 \pm 40)$ eV nm^{-3} from an analysis of Bragg reflection data.

In the case of cadmium, there has been a recent estimate of the antisymmetric potential parameter from a measurement on a quasi-forbidden reflection by Merisalo, Peljo & Soininen (1978). Also, a single-crystal X-ray investigation of cadmium has been carried out by Rossmanith (1978) and a set of structure factors published (Rossmanith, 1978, Supplementary Publication). The data of Rossmanith have been reanalysed by the present author with a one-particle potential to determine the anharmonic parameters and to compare the parameter for the antisymmetric component with that found by Merisalo, Peljo & Soininen (1978).

Theory

Cadmium crystallizes in a hexagonal structure, with space group $P6_3/mmc$. The lattice constants given by Rossmanith (1978) are $a = 2{\cdot}977$ and $c = 5{\cdot}612$ Å,

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