ganophyllite raises several interesting questions, the most important being the apparent absence of any of the simpler structures described above. This would suggest that some form of ordering scheme exists, giving rise to relatively long-range structural control. Variation of structural form with chemical composition has long been known in micas and other layered silicates (see, for example, Radoslovich, 1963) and the complex composition of ganophyllite, given by Smith & Frondel (1968) as $(K_{1 \cdot 87}Na_{2 \cdot 29})(Mg_{0 \cdot 16}Ca_{0 \cdot 65}Pb_{0 \cdot 03}Mn_{16 \cdot 14}Fe_{0 \cdot 36})O_{52 \cdot 6}(OH)_{35 \cdot 4}$ appears to imply a capacity for chemical substitution. Whether such a variation could be detected by conventional electron-microprobe methods is a matter of speculation, but compositional differences have been investigated in this way in zussmanite (Jefferson, 1976) and the detection of similar chemical substitution in chloritoid (Crawford, Jefferson & Thomas, 1978) by energy-dispersive analysis in the electron microscope, suggests a possible avenue of further investigation.

References

Cochran, W. & Howells, E. R. (1954). *Acta Cryst.* **7**, 412–415.

Crawford, E. S., Jefferson, D. A. & Thomas, J. M. (1977). *Acta Cryst.* A**33**, 548–553.

Crawford, E. S., Jefferson, D. A. & Thomas, J. M. (1978). In preparation.

Eggleton, R. A. (1972). *Mineral. Mag.* **38**, 693–711.

Eggleton, R. A. & Bailey, S. W. (1965). *Clays Clay Miner.* **13**, 49–63.

Hamberg, A. (1890). *Geol. Foeren. Stockholm. Foerh.* **12**, 586–598.

Jefferson, D. A. (1976). *Am. Mineral.* **61**, 470–483.

Jefferson, D. A. & Bown, M. G. (1973). *Nature* (*London*) *Phys. Sci.* **245**, 43–44.

Lopes-Vieira, A. & Zussman, J. (1969). *Mineral. Mag.* **37**, 49–60.

Radoslovich, E. W. (1963). *Am. Mineral.* **48**, 348–367.

Smith, M. L. & Frondel, C. (1968). *Mineral. Mag.* **36**, 893–913.

Acta Cryst. (1978), A**34**, 497–500

X-ray Measurement of the Root-Mean-Square Displacement of the Atoms in Cadmium Single Crystals

By Elisabeth Rossmanith

Mineralogisch-Petrographisches Institut der Universität Hamburg, 2000 *Hamburg* 13, *Grindelallee* 48, *Federal Republic of Germany*

(*Received* 18 *October* 1977; *accepted* 9 *February* 1978)

The root-mean-square displacements u_a and u_c of the cadmium atoms in single crystals in the **a** and **c** directions, respectively, were determined by the use of Bragg intensities obtained with Mo $K\alpha$ radiation. The results [$u_a = 0 \cdot 121$ (1), $u_c = 0 \cdot 196$ (1) Å] are compared with other X-ray measurements.

Introduction

As stated in Rossmanith (1977) (R-77 hereinafter) the thermal parameters obtained by the use of least-squares fits of observed and calculated structure factors are in satisfactory agreement with values obtained by other methods, if (*a*) the substances consist of heavy atoms and are highly symmetrical, so reducing the six thermal parameters to one or two independent parameters, and if (*b*) the corrections for absorption, extinction and TDS are properly made.

It was shown in R-77 that in the case of Zn, in which there is high extinction, the results obtained for u_a and u_c, the root-mean-square displacements in the **a** and **c** directions of the crystal, were in good agreement with those obtained by Skelton & Katz (1968), measured in the temperature range 4·85 to 600 K.

This encouraged the author to determine the root-mean-square displacement of Cd with the help of least-squares procedures. For Cd, where extinction is severe, mainly because of the high atomic number of Cd, again it can be shown that the values of the thermal parameters are strongly affected by extinction correction.

Experimental

Two spherical Cd single crystals (99·9999% Cd) were supplied by Guse (1971). The experimental procedure is very similar to that described in R-77. The main features of the measurement are shown in Table 1.

All reflexions were measured four times. For each reflexion the error in the measured intensity, ΔI, was calculated, taking into account the variance from

Table 1. *Main experimental features*

Radius of sphere 1 : $R_s^1 = 0.00325 \mp 0.00010$ cm
Radius of sphere 2 : $R_s^2 = 0.00307 \mp 0.00010$ cm
$\mu R_s^1 = 0.77$
$\mu R_s^2 = 0.73$
Space group: $P6_3/mmc$ (No. 194)
Special positions of the two atoms per unit cell: 0,0,0 and $\frac{2}{3},\frac{1}{3},\frac{1}{2}$
Cell constants (estimated by least-squares analysis of measured and calculated Bragg angles): $a = b = 2.977$ (1) Å $c = 5.612$ (2) Å
Diffractometer used: Hilger & Watts, with graphite monochromator
Wavelength used: Mo $K\alpha$
$\sin\theta/\lambda$ range: <0.81 Å^{-1}
Scan: $\theta/2\theta$
Number of measured reflections: 368 (one half of the hemisphere)
Number of symmetrically independent reflections: 49

counting statistics and systematic errors of the measurement, as the filter-factor error and discrepancies in reference measurements (the intensity of the reference reflection was measured several times during the measurement of the Bragg intensities). For further calculations the Bragg intensities, following a reference measurement, were multiplied by a factor calculated by dividing the intensity of the first reference measurement by the actual reference intensity.

Corrections applied to the intensity data

(*a*) *Lp and absorption correction.* The intensities of both spheres were corrected for absorption with the absorption factor A^* for spheres of Weber (1969). The Lp correction was applied with the formula given by Azaroff (1955) in the case where the scattering planes of the monochromator and the sample are mutually perpendicular.

(*b*) *TDS correction.* The intensity data for sphere 2 were corrected for TDS with the formula: $I_{\text{corr}} = I_{\text{obs}}/(1 + \alpha)$, where I_{corr} and I_{obs} are the corrected and observed intensities and α is the TDS-correction term. For TDS correction a modified version (de With & Mulder, 1975) of the computer program *TDS*2 by Stevens (1974) was used. The program is applicable to crystals of any symmetry type and calculates α, including both one and two-phonon scattering. The program was modified by the author to allow for the geometry of the Hilger & Watts diffractometer and to give as output, reflection cards which can be used as input cards for the least-squares program *LINEX*74. As necessary for input to *LINEX*74, these cards contain the vector components of the vector parallel to the incident beam and the vector normal to the plane containing the incident and diffracted beams.

The α values were calculated for one-phonon scattering only, using the values of the elastic constants in hexagonal Cd: $c_{11} = c_{22} = 11.6$, $c_{33} = 5.1$, $c_{44} = c_{55} = 1.95$, $c_{66} = (c_{11} - c_{12})/2 = 3.69$, $c_{12} = 4.23$, $c_{13} = c_{23} = 4.14$ in 10^{11} dyn cm^{-2} (Landolt–Börnstein, 1966) and the scan width SWD $= (1.1 + 0.35 \tan\theta)°$. The aperture of both the horizontal and vertical detectors was 0.5°. Because of the small detector aperture the TDS correction is small, resulting in $\alpha < 0.02$ ($\alpha_{\max} = \alpha_{4\bar{4}2} = 0.0184$, $\alpha_{\min} = \alpha_{010} = 0.00003$).

(*c*) *Extinction correction.* For extinction correction the two least-squares programs *ORXFLS*3 and *LINEX*74 were used. Both programs are modified versions of *ORFLS* by Busing, Martin & Levy (1962). The extinction formulae used in these two programs are collated in R-77. Both programs were modified by the author to allow for the use of a diffractometer with monochromator [equation (3) in R-77]. As input data for the least-squares routines the atomic form factor for Cd^{2+} of Cromer & Mann (1968) and the anomalous dispersion coefficient for Cd of Cromer & Libermann (1970) were used. Because of the symmetry of the lattice the thermal parameters are constrained: $\beta_{11} = \beta_{22}$, $\beta_{12} = \beta_{11}/2$, $\beta_{23} = \beta_{13} = 0$ (Peterse & Palm, 1966). The extinction was severe reaching a minimum value $y_{\min} = y_{200} = 0.375$.

Results

The refinement was first carried out with the scale factor and the two independent temperature parameters β_{11} and β_{33} allowed to vary. The results of this refinement are tabulated in the left-hand part of Table 2. Subsequently, the isotropic extinction parameter was varied together with the scale factor and the temperature parameters (middle part of Table 2). At the end of the refinement by least-squares analysis the scale factor, the two independent temperature parameters and the six anisotropic extinction parameters were refined simultaneously (right-hand part of Table 2).

In *ORXFLS*3 type I anisotropic extinction was used; in *LINEX*74 the Thornley & Nelmes (1974) model of extinction anisotropy, the Lorentzian distribution for mosaic spread and the mean diffracting unit cross section are assumed, as this combination gives the best fit to the available data (as concluded by R-77).

In the calculations on the intensity data of sphere 2, corrected for TDS, the results for the crystallographic R values defined as $R = \sum(||F_o| - |F_c||/|F_o|)$ for these three steps of refinement are 0.069, 0.024 and 0.018. Using the significance test of Hamilton (1965), we can therefore reject the hypothesis that extinction correction is isotropic at a significance level of $\alpha = 0.005$. As pointed out in R-77, the u^2 values are too small if extinction correction is not applied to the intensity data. The difference in the u^2 values between the results for isotropic and anisotropic extinction is not as drastic in the case of our Cd sphere as in the case of our Zn sphere (R-77). This can be explained by the fact that the ratio of the extinction parameters T_{11} and T_{33} is much smaller in the case of Cd ($T_{11}/T_{33} \sim 2$) than in the case of our Zn sphere ($T_{11}/T_{33} \sim 10$). Comparing

Table 2. *Results of refinement*

	Program used	Without extinction			With isotropic extinction			With anisotropic extinction		
		R %	u_a^2 (Å^2) $\times 10^4$	u_c^2 (Å^2) $\times 10^4$	R %	u_a^2 (Å^2) $\times 10^4$	u_c^2 (Å^2) $\times 10^4$	R %	u_a^2 (Å^2) $\times 10^4$	u_c^2 (Å^2) $\times 10^4$
Sphere 1	*ORXFLS*3	9·8	20 (8)	223 (10)	2·4	146 (8)	394 (8)	2·1	141 (3)	386 (2)
Sphere 1	*LINEX*74	9·9	21 (8)	222 (10)	–	–	–	1·2	141 (3)	387 (3)
Sphere 2	*LINEX*74	6·7	65 (5)	298 (7)	2·5	133 (5)	394 (5)	1·8	139 (3)	382 (3)
Sphere 2 with TDS	*LINEX*74	6·9	69 (6)	300 (7)	2·4	139 (5)	396 (5)	1·8	146 (3)	385 (3)

the calculations with anisotropic extinction correction applied, satisfactory agreement between the results for the u^2 values of sphere 1 and sphere 2 is obtained, the differences being within the error limits.

The results on u^2 obtained with *ORXFLS*3 are in agreement with those obtained with *LINEX*74. This shows (as concluded in R-77) that the u^2 values are not sensitive to the particular extinction model used.

As expected, the u^2 values are greater for the calculations with TDS correction applied (last line in Table 2) than those without (penultimate line).*

Discussion

X-ray measurements of the root-mean-square displacement in Cd single crystals have not been found in the literature. Brindley & Ridley (1939) measured the intensities of X-ray reflections from Cd powder at 86 and 293 K. Walford, Carron & Schoeffel (1968) measured the intensities of four X-ray reflections from Cd powder in the temperature range 77 to 293 K.

Using the formulae

$$\cos \psi = (la/c)[4(h^2 - hk + k^2)/3 + (la/c)^2]^{-1/2},$$

where ψ is the angle between the c axis of the crystal and the normal of the reflecting plane, and

$$u_{hkl}^2 = u_a^2 \sin^2 \psi + u_c^2 \cos^2 \psi,$$

we can compare the results of both these papers with the present results. Table 3 shows the values of u^2 for some ψ values including all four reflections measured by Walford *et al.* (1968). The average value of u^2, used in Table 3, is defined as

$$u_{\rm av}^2 = (1/3)(u_c^2 + 2u_a^2).$$

In the case of Walford *et al.* (1968) the weighted mean given in their paper is used for comparison with $u_{\rm av}^2$.

A comparison of the three sets of data reveals some large discrepancies. Although the average value of u^2 for each set is of similar order of magnitude, the differences are too great to be ignored. Brindley & Ridley (1939) as well as the present work have ascertained that the temperature effect in Cd is anisotropic, u_c ($\psi = 0°$) being larger than u_a ($\psi = 90°$). $u^2(\psi)$ therefore decreases monotonically with ψ. Walford *et al.* (1968) stated that they had not observed anisotropy of the temperature effect. Although their method is adequately described, their original measurements are not given, and it is therefore not possible to assess the reason for the relatively large discrepancies in the calculated data when compared with those of the other two sets. The difference between the results obtained by Brindley & Ridley (1939) and the present paper may have two causes. First, the relatively large difference between the results for u_c may be because Brindley & Ridley measured 11 symmetrically independent reflections, 9 of them having $\psi > 55°$, none of them having $\psi = 0°$, whereas in the present paper 49 symmetrically independent reflexions were observed, 20 of them with $\psi < 45°$, 4 of them with $\psi = 0°$. Second, the differences in u_a as well as in u_c may be due to the method Brindley & Ridley (1939) used to place their data on an absolute scale, as the values of u_a and u_c are sensitive to the ratio between the relative and absolute intensities.

Finally, it is of interest to compare the ratio u_c/u_a for

Table 3. *Comparison of the present results with previous work*

		u_{hkl}^2 (Å^2)		
$h\,k\,l$	Ψ	1	2	3
2 0 0	90·0°	0·140	–	0·0146 (3)
2 1 1	80·1	0·0146	0·0231 (8)	0·0153
3 0 2	73·0	0·0156	0·0231 (8)	0·0166
2 1 2	70·9	0·0160	0·0173 (10)	0·0172
1 2 3	64·0	0·0177	0·0158 (9)	0·0192
0 0 6	0·0	0·0330	–	0·0385 (3)
		$u_{\rm av}^2 = 0{\cdot}0203$	0·0211 (7)*	$u_{\rm av}^2 = 0{\cdot}0226$ (3)

References: (1) Brindley & Ridley (1939). (2) Walford *et al.* (1968). (3) Present work.

* Weighted mean.

---

* A list of F_o, F_c, y and α values for sphere 2 has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33404 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Zn and Cd, as done by Brindley & Ridley (1939). In Table 4 the mean of the results No. 17 and 21 of Table 5 in R-77 for the root-mean-square displacements of the atoms in Zn is used to calculate the u_c/u_a ratio of Zn. The ratio is compared with the Cd ratio of the present work and with that of Brindley & Ridley (1939).

Table 4. u_c/u_a *ratio for* Zn *and* Cd

	Zn (R-77)	Cd (present work)	Cd (Brindley & Ridley, 1939)
u_c/u_a	1·63 (2)	1·62 (2)	1·54

Zn and Cd have similar electronic structures (Zn: $3d^{10}4s^2$; Cd: $4d^{10}5s^2$) and are both built up of an h.c.p. lattice with an anomalously large c/a ratio (ideal h.c.p.: $c/a = 1{\cdot}633$; Zn: 1·853, Cd: 1·885). If we therefore assume a similar vibrational behaviour for Zn and Cd, the ratio u_c/u_a obtained in the present work suggests a more satisfactory result.

References

AZAROFF, L. (1955). *Acta Cryst.* **8**, 701–704.

BRINDLEY, G. W. & RIDLEY, P. (1939). *Proc. Phys. Soc. London*, **51**, 73–80.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305, Oak Ridge National Laboratory, Tennessee.

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–342.

GUSE, W. (1971). *Über die Herstellung metallischer Teilchen im Grössenbereich des Staubes.* Thesis, Univ. Hamburg.

HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510.

Landolt–Börnstein (1966). *Zahlenwerte und Funktionen aus Naturwissenschaften und Technik.* Vol. III, part 1. Berlin: Springer.

PETERSE, W. J. A. M. & PALM, J. H. (1966). *Acta Cryst.* **20**, 147–150.

ROSSMANITH, E. (1977). *Acta Cryst.* A**33**, 593–601.

SKELTON, E. & KATZ, L. (1968). *Phys. Rev.* **171**, 801–808.

STEVENS, E. D. (1974). *Acta Cryst.* A**30**, 184–189.

THORNLEY, F. R. & NELMES, R. J. (1974). *Acta Cryst.* A**30**, 748–757.

WALFORD, L. K., CARRON, G. J. & SCHOEFFEL, J. A. (1968). *Mater. Res. Bull.* **3**, 911–918.

WEBER, K. (1969). *Acta Cryst.* B**25**, 1174–1178.

WITH, G. DE & MULDER, R. A. P., (1975). Private communication.

Acta Cryst. (1978). A**34**, 500–505

Anharmonic Contributions to Bragg Diffraction.
I. Copper and Aluminium

BY C. J. MARTIN* AND D. A. O'CONNOR

Department of Physics, University of Birmingham, England

(*Received* 12 *September* 1977; *accepted* 6 *October* 1977)

Anharmonic contributions to the atomic motion in copper and aluminium single crystals have been determined from measurements of the elastic scattering of recoil-less γ-rays at temperatures up to 1200 K for copper and 900 K for aluminium. The results are compared with theoretical predictions.

Introduction

The thermal motion of the atoms in a crystal lattice reduces the intensity of the elastically diffracted Bragg X-ray peaks while increasing the intensity of thermal diffuse scattering (TDS). If the magnitude of a particular Bragg reflection is recorded as a function of temperature, information about the amplitudes of the atomic vibrations can be found and estimates can, in principle, be made of their anharmonicity. However, in the regions where the anharmonic effects are most significant, namely for the higher-order Bragg reflections at elevated temperatures, the TDS makes a substantial contribution to the total scattered intensity. The TDS results from interactions between the incident

---

* Present address: Department of Medical Physics, University of Aberdeen, Scotland.