present; see especially Fig. 6); and so the final, 'thick' corundum layer may well have lateral corrugations also. But the end result is a thin lamella of corundum-like Ti_2O_3 coherently intergrown with $TiO_{2-\delta}$ (where δ may be very small indeed, down to zero in regions close to CSP's). This, we suggest, is the explanation of the wide, dark bands at the CSP's in Figs. 4, 5 and 6.

We are grateful to Mr Peter Barlow for assisting with the electron microscopy. One of us (LCO-D) wishes to thank the Research School of Chemistry for a Visiting Fellowship which enabled this work to be completed.

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On Anharmonicity in Zinc and Cadmium

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(*Received* 16 *December* 1982; *accepted* 19 *January* 1984)

Abstract

X-ray diffraction data on Zn [Rossmanith (1977). *Acta Cryst.* A**33**, 593–601] and Cd [Rossmanith (1978). *Acta Cryst.* A**34**, 497–500] have been reanalyzed using a temperature factor based on an anharmonic one-particle potential to fourth order for the atoms in the crystal. Because of the strong correlation of the harmonic parameters α_{20}, β_{00} and the anharmonic parameters α_{33}, α_{40}, β_{20}, γ_{00}, the harmonic parameters of Zn were calculated using an approximate model. It is shown that for one set of harmonic parameters the results for the anharmonic parameters are ambiguous, giving a distribution of compatible values for the fourth-order anharmonic parameters. To check the influence of systematic errors on the anharmonic parameters introduced into calculations by absorption and extinction correction the results for two Cd single-crystal samples are compared. For the third-order parameter α_{33}, which rules the antisymmetric part of the thermal motion, comparable values are found for both Cd samples. The results on the fourth-order anharmonic parameters for the two Cd crystals are not consistent.

Introduction

From their X-ray data on Zn Skelton & Katz (1968) evaluated the mean-square displacements $\langle u_a^2\rangle$ and $\langle u_c^2\rangle$ in the **a** and **c** directions of the crystal respectively. Comparing their results with calculated values of Barron & Munn (1967) in quasiharmonic approximation using thermodynamic data, they concluded that the high-temperature discrepancy in $\langle u_a^2\rangle_T$ may be caused by constant-volume anharmonic effects, whereas $\langle u_c^2\rangle_T$ is consistent with theoretical values.

The Mössbauer technique was used by Albanese, Deriu & Ghezzi (1976) to obtain the anharmonic contribution to the Debye–Waller factor of Zn for vibrations parallel to the *c* axis from the temperature dependence of integrated Bragg intensities. In partial disagreement with the results of Skelton & Katz (1968), they found an anharmonic contribution to the atomic vibration in the **c** direction, not consistent with predictions of quasiharmonic theory.

Merisalo & Larsen (1977) used elastic thermal neutron data from a single crystal of Zn measured at 295 K to estimate the anharmonicity of lattice vibrations, treating the crystal as a system of independent

0108-7681/84/030244-06$01.50

Table 1. *Previous work on the anharmonic parameters of the* Zn *and* Cd *atoms in the special position* $(\frac{1}{3}, \frac{2}{3}, \frac{3}{4})$ (*site symmetry* $\bar{6}m2$)

α_{20}, β_{00}: harmonic temperature parameters defined in relation (2).
α_{33}, α_{40}, β_{20}, γ_{00}: anharmonic temperature parameters defined by Merisalo & Larsen (1977).
M & L: Merisalo & Larsen.
M, J & K: Merisalo, Järvinen & Kurittu (1978).
M, P & S: Merisalo, Peljo & Soininen (1978).

	Reference	α_{20}	β_{00}	α_{33}	α_{40}	β_{20}	γ_{00}
		($\times 10^{-12}$ erg Å^{-2})*		($\times 10^{-12}$ erg Å^{-3})	($\times 10^{-12}$ erg Å^{-4})	($\times 10^{-12}$ erg Å^{-4})	($\times 10^{-12}$ erg Å^{-4})
Zn	M & L (1977) (model 1)	−0·766 (10)	1·511 (10)	0	2·77 (15)	−1·32 (15)	−0·04 (10)
	M & L (1977) (model 2)	−1·109 (10)	1·841 (10)	0	1·33 (15)	6·52 (20)	−6·13 (20)
	M, J & K	—	—	−1·5 (3)	—	—	—
	M & L (1979)	−1·109 (10)	1·841 (10)	−1·8 (3)	0·25 (28)	7·36 (28)	−6·27 (14)
Cd	Field (1982) (with extinction)	−0·658 (2)	1·157 (2)	−0·041 (20)	—	—	0·149 (30)
	Field (1982) (without extinction)	−0·691 (2)	1·226 (2)	−0·091 (26)	—	—	—
	M, P & S	—	—	−0·130 (20)	—	—	—

* 1 erg = 10^{-7} J.

anharmonic oscillators, whereby the real crystal potential is replaced by an effective one-particle potential. This potential is expanded in a power series as a function of the Cartesian coordinates u_1, u_2, u_3 of the displacement $\mathbf{u}$ from the equilibrium lattice sites, where terms up to the fourth order have been retained.

Because of the site symmetry of the Zn atoms in the hexagonal close-packed structure, the ten independent third-rank coefficients of the expansion reduce to the anharmonic parameter α_{33} and the 15 fourth-rank coefficients reduce to three independent anharmonic parameters α_{40}, β_{20}, γ_{00}. The six second-rank coefficients of the expansion reduce to the harmonic parameters α_{20} and β_{00}. Merisalo & Larsen (1977) estimated the anharmonic parameters for two models: In model (1) the harmonic parameters α_{20}, β_{00} are those obtained in the harmonic approximation, in model (2) these parameters are determined from the quasiharmonic calculations of Barron & Munn (1967). These results are collated in Table 1. Merisalo, Järvinen & Kurittu (1978) reported results of an X-ray study of the almost forbidden reflexions in Zn crystals, which can be interpreted to be due to anharmonicity of lattice vibrations. For the anharmonic parameter α_{33}, which is determined by the antisymmetric behavior of the atomic vibrations in the crystal, they obtained the value given in Table 1.

Merisalo & Larsen (1979) reconsidered their elastic neutron scattering data using a slightly different estimate for the standard deviation of the variable parameters, yielding a different set of anharmonic parameters, given also in Table 1. α_{33} is now in fairly good agreement with the results of Merisalo, Järvinen & Kurittu (1978).

A site-symmetrized Fourier invariant treatment of anharmonic temperature factors derived within the framework of the effective one-particle potential formalism was developed by Kurki-Suonio, Merisalo & Peltonen (1979) and applied to the neutron diffraction data on Zn by Merisalo & Larsen (1977).

Vahvaselkä (1980) reanalyzed the thermal neutron diffraction data of Merisalo & Larsen (1977) using the direct-analysis formalism of Kurki-Suonio (1977*a*, *b*). To consider anharmonicity site-symmetrized expansions of real spherical harmonics for the nuclear density distribution are used. He concluded that on the basis of the data used the existence of anharmonicity of thermal motion in Zn is qualitatively well established. X-ray measurements on Zn, Cd and Mg from 295 K to the melting points are given by Pathak & Desai (1981). Their values given for the mean-square displacement of Zn exceed those of Skelton & Katz (1968) for temperatures above 350 K, even though indicating anharmonicity of thermal vibration.

From all this previous work it can be concluded that anharmonicity in Zn is well established. The quantitative results found by the different investigators, however, differ substantially. One purpose of the present work was therefore to prove the reliability of anharmonic parameters yielded from X-ray intensity data. Recently, Field (1982) reanalyzed X-ray diffraction data on Cd by Rossmanith (1978), considering the temperature factor as derived from an anharmonic one-particle potential. He concluded that the anharmonic model fits the data significantly better than the harmonic model and that the anisotropic extinction correction applied by Rossmanith (1978) resulted in an overcorrection of the intensities of the low-angle data having an effect on the antisymmetric anharmonic parameter α_{33}. The results are given also in Table 1. The value of α_{33} is compared with the results obtained by Merisalo, Peljo & Soininen (1978) from an investigation of the 'quasi forbidden' reflexion 303.

The X-ray diffraction measurements reported in Rossmanith (1978) have been performed on two single-crystal spheres, resulting in two data sets, which are differently affected by absorption and extinction. Therefore it seemed worth comparing the anharmonic recalculations of the two measurements to check the presumptions of Field (1982).

Table 2. *The harmonic and anharmonic temperature parameters for the* Zn *atom in the special position* $(\frac{1}{3}, \frac{2}{3}, \frac{3}{4})$

α_{20}, β_{00}: harmonic temperature parameters defined in relation (2).
α_{33}, α_{40}, β_{20}, γ_{00}: anharmonic temperature parameters defined by Merisalo & Larsen (1977).
The number in the last column gives the step of calculation mentioned in the text.

	α_{20} ($\times 10^{-12}$ erg Å^{-2})	β_{00} ($\times 10^{-12}$ erg Å^{-2})	α_{33} ($\times 10^{-12}$ erg Å^{-3})	α_{40} ($\times 10^{-12}$ erg Å^{-4})	β_{20} ($\times 10^{-12}$ erg Å^{-4})	γ_{00} ($\times 10^{-12}$ erg Å^{-4})	Step
Model (*a*)							
	−0·869 (27)	1·654 (35)	0·0	0·02 (42)	0·05 (33)	−0·05 (11)	2
			−0·30 (25)	0·02 (42)	0·06 (33)	−0·06 (11)	3
			0·0	0·05 (54)	0·03 (50)	−0·04 (27)	4
			−0·31 (30)	0·05 (50)	0·04 (50)	−0·05 (25)	5
Model (*b*)							
	−0·866 (26)	1·708 (30)	0·0	0·35 (51)	−0·11 (38)	−0·46 (12)	2
			−0·33 (28)	0·34 (51)	−0·10 (38)	−0·47 (12)	3
			0·0	0·31 (66)	−0·01 (57)	−0·56 (31)	4
			−0·33 (34)	0·32 (66)	0·00 (58)	−0·57 (31)	5

Evaluation of the temperature parameters of Zn

The Bragg intensities measured with Mo $K\alpha$ radiation in the $\sin\vartheta/\lambda$ range $\leq 0{\cdot}81$ Å^{-1} (ϑ being the Bragg angle and λ the wavelength of the X-rays) by Rossmanith (1977) were corrected for thermal diffuse scattering (TDS). The largest TDS contribution to the intensities was found to be 1% for the 017 reflexion. Re-refinement of these corrected intensities in the harmonic approximation resulted in

$$\begin{aligned}\langle u_a^2\rangle &= 0{\cdot}0098\,(2)\ \text{Å}^2\\ \langle u_c^2\rangle &= 0{\cdot}0260\,(2)\ \text{Å}^2\end{aligned}\qquad(1)$$

and a goodness-of-fit R value of 0·0067, R being defined by $R=\sum|F_o-F_c|/\sum F_o$. (F_o and F_c are the observed and calculated structure factors.)

1. *The harmonic parameters* α_{20}, β_{00}

Because of the strong correlation between the harmonic and anharmonic parameters (Merisalo & Larsen, 1977), the harmonic parameters were not refined simultaneously with the anharmonic ones, but they were calculated using two models:

(*a*) Following Merisalo & Larsen (1977) in their model (1), for model (*a*) the mean-square displacements given in equations (1) were used for evaluation of the harmonic parameters α_{20} and β_{00}. The relation between the harmonic parameters β_{11}, β_{33}, the mean-square displacements $\langle u_a^2\rangle$, $\langle u_c^2\rangle$ and the second-order parameters α_{20} and β_{00} is given by

$$\begin{aligned}\beta_{11} &= 2\pi^2\frac{\langle u_a^2\rangle\times 4}{3a^2}=\frac{4\pi^2k_BT}{3a^2(\beta_{00}-\frac{1}{2}\alpha_{20})}\\ \beta_{33} &= 2\pi^2\frac{\langle u_c^2\rangle}{c^2}=\frac{\pi^2k_BT}{c^2(\beta_{00}+\alpha_{20})},\end{aligned}\qquad(2)$$

where a and c are the lattice constants, T is the absolute temperature and k_B is Boltzmann's constant.

Because the 'harmonic parameters' evaluated in this way include anharmonic parts of the thermal motion, the results of these harmonic and anharmonic parameters of model (*a*) have questionable physical meaning.

Paying regard to Fig. 4 of Rossmanith (1980), the harmonic parameters α_{20} and β_{00} should be calculated being due only to the harmonic part of the thermal vibrations and the anharmonic part of the thermal vibration, described by the anharmonic parameters α_{33}, α_{40}, β_{20}, γ_{00}, and should fill in the gap between curve 5 of Fig. 4 (calculated mean-square displacement in harmonic approximation) and the experimental values given by Skelton & Katz (1968).

Therefore, in model (*b*) the harmonic part of $\langle u_a^2\rangle$ and $\langle u_c^2\rangle$ was calculated approximately.

(*b*) For model (*b*) the approach proposed by Albanese, Deriu & Ghezzi (1976) was used for evaluation of the harmonic part of the mean-square displacements. Computational details are given in the Appendix.* The results obtained are

$$\begin{aligned}u_a^2 &= 0{\cdot}0095\,(2)\ \text{Å}^2\\ u_c^2 &= 0{\cdot}0242\,(2)\ \text{Å}^2.\end{aligned}\qquad(3)$$

The corresponding values for α_{20}, β_{00} are given in the second row of Table 2.

Bearing in mind the many approximations used in deducing $\langle u_a^2\rangle$ and $\langle u_c^2\rangle$ in model (*b*) the average value

$$\langle u_{\rm av}^2\rangle=\tfrac{1}{3}(2\langle u_a^2\rangle+\langle u_c^2\rangle)=0{\cdot}0144\,(2)\ \text{Å}^2$$

is in fairly good agreement with the theoretical value $\langle u_{\rm av}^2\rangle=0{\cdot}0140$ Å^2, obtained in the harmonic approximation by Rossmanith (1980) *from the frequency* spectrum of the atomic motion in Zn.

2. *The anharmonic parameters* α_{33}, α_{40}, β_{20}, γ_{00}

The program *LINEX*74 was modified to allow the alternative use of the harmonic temperature factor or

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* The Appendix and Tables 4(*a*), 4(*b*), 5, 6, 7(*a*) and 7(*b*) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39168 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the anharmonic temperature factor defined in equations (1) to (8) of Merisalo & Larsen (1977). The analysis was performed in five steps.

In the first three steps the TDS- and extinction-corrected intensities were used as observed ones. In the first step the *R* value was calculated for a large number of combinations of the parameters α_{40}, β_{20}, γ_{00} with α_{33} set to zero. In Tables 4(*a*) and 4(*b*)* some of the results of this analysis are given. From Tables 4(*a*) and 4(*b*) it can be seen that for many combinations of the fourth-order anharmonic parameters the same small *R* value (0·0064) is reached. The values $\langle u_a^2\rangle_{\rm anha}$ and $\langle u_c^2\rangle_{\rm anha}$ given in Table 4(*b*) are the second moments defined on page 354 of Merisalo & Larsen (1977), calculated for the α_{40}, β_{20} combination with the smallest *R* value in the appropriate row. In the second step, assuming $\alpha_{33} = 0{\cdot}0$, the fourth-order anharmonic parameters were refined. The results are given in Table 2. In the third step the third- and fourth-order anharmonic parameters were refined simultaneously. The results are given also in Table 2. The observed and calculated structure factors obtained in this step are given in Table 6.*

The calculations of steps four and five correspond to those of steps two and three differing in that the TDS-corrected intensity data without extinction correction applied were used as input. The anharmonic parameters, the extinction parameters and the scale factor were refined simultaneously giving the results shown also in Table 2. The *R* value reached was 0·0067.

Comparing the results of steps 2 and 4 or 3 and 5 for model (*a*) we can conclude that the influence of the extinction correction on the values of the anharmonic parameters is negligible in this analysis giving comparable small values for the anharmonic parameters in the case when extinction parameters are refined simultaneously with the anharmonic ones as well as when extinction-corrected intensities are used as input data for least-squares refinement. This result is not surprising in view of the same small *R* value (0·67%) for the least-squares refinement in harmonic as well as in anharmonic approximation.

Comparing the results of steps 2 and 4 for model (*b*) it can be seen from Table 4(*b*) that refining extinction and anharmonic parameters simultaneously results in a combination of anharmonic parameters, which is nearly the same as one of those many combinations found in step 1 using extinction-corrected intensities as input data.

The small influence of the extinction correction on the values of the anharmonic parameters in the present analysis of the X-ray intensities is confirmed by the fact that the only correlation between the extinction parameters and anharmonic parameters found in least-squares analysis giving a correlation coefficient greater than 0·5 is found for the parameters γ_{00}–g_{33} (for definition of g_{33} see Rossmanith, 1977) to be 0·63 for model (*a*) as well as for model (*b*).

A recalculation of the anharmonic parameters given by Merisalo & Larsen (1977) using their neutron intensity data shows a similar distribution of compatible values of the fourth-order parameters as given in Tables 4(*a*) and 4(*b*), the spread of the distribution being as significant as in the X-ray case.

Evaluation of the temperature parameters of Cd

The results of the harmonic and anharmonic refinements are summarized in the Tables 3(*a*) and 3(*b*). The symbols used are defined in the glossary. In Table 5* the harmonic and anharmonic refinements are compared *via* Hamilton's (1965) ratio test. In Tables 7(*a*) and 7(*b*)* the observed and calculated structure factors for data sets 2*g* and 6*g* are given.

Discussion

Comparison of the results given in Tables 1, 2, 3(*a*) and 3(*b*) shows disagreement especially in the fourth-order anharmonic parameters. In the case of Zn the disagreement in the fourth-order parameters between the results of models (*a*) and (*b*) (Table 2) may partly be due to the fact that different second-order parameters are used in the refinement. In the harmonic approximation where solely second-order terms in the expansion of the potential are taken into account the equipotential contours of the potential of the atoms in the crystal are ellipsoids. Considering fourth-order terms in the potential expansion causes distortion of these ellipsoids, namely positive α_{40} produces hardening of the potential in the basal plane as well as in the **c** direction, positive β_{20} produces softening in the basal plane and hardening in the **c** direction, positive γ_{00} produces hardening in the basal plane as well as in the **c** direction and the opposite is true for the negative parameters. Comparing the results of the fourth-order parameters of model (*a*), which are nearly zero [the associated *R* value (0·0066) being insignificantly smaller than that reached in the harmonic approximation], with those of model (*b*), one may conclude that the fourth-order parameters obtained in refinement are fitted and balanced so as to enlarge the ellipsoids of the equipotential contours belonging to (3) resulting very nearly in the ellipsoids belonging to (1). The values obtained for $\langle u_a^2\rangle_{\rm anha} = 0{\cdot}0098$ Å^2 and $\langle u_c^2\rangle_{\rm anha} = 0{\cdot}0261$ Å^2 given in Table 4(*b*) support this supposition. In the case of Cd the different magnitude of the systematic errors introduced into calculations by absorption, TDS and extinction

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* See deposition footnote.

* See deposition footnote.

Table 3. *Results of the harmonic and anharmonic refinements*

No.: number of refinement.

$N = 342$(CD1TDS), 368(CD2TDS): all reflexions up to $\sin\theta/\lambda = 0{\cdot}79$ Å^{-1} (CD1TDS), $= 0{\cdot}81$ Å^{-1}(CD2TDS) used.

$= 194$(CD1TDS), 300(CD2TDS): all reflexions with extinction factor $y > 0{\cdot}9$ (calculated in the refinement with all reflexions used).

nv = 3: scale factor and harmonic temperature parameters β_{11}, β_{33} refined simultaneously, no extinction correction applied.

= 9: scale factor, β_{11}, β_{33} and six anisotropic extinction parameters refined simultaneously.

= 11: scale factor, six extinction parameters and the anharmonic temperature parameters α_{33}, α_{40}, β_{20}, γ_{00} refined simultaneously.

= 5: scale factor and four anharmonic parameters refined simultaneously; no extinction correction applied.

η_i:mosaic spread.

$\sigma = [\sum w_i(F_o - F_c)^2/(N - \text{nv})]^{1/2}$.

$w_i = 1/\sigma_i^2$.

σ_i^2: variance of the structure factor F_o.

DS: number of refinement from which $\langle u_a^2\rangle$ and $\langle u_c^2\rangle$ is taken for calculation of α_{20}, β_{00}.

The units of the temperature parameters are the same as in Table 1.

(*a*) Harmonic-refinement results

Dataset name	No.	N/nv	$\langle u_a^2\rangle$ Å^2 ($\times 10^4$)	$\langle u_c^2\rangle$ Å^2 ($\times 10^4$)	η_1	η_2 (seconds)	η_3	$R(\times 10^4)$	σ
CD1TDS	2	342/9	143 (3)	388 (3)	6·0	5·9	2·1	115	3·30
	2δ	194/3	131 (3)	367 (3)	—	—	—	156	2·42
	2ε	194/9	137 (3)	383 (3)	5·6	6·0	2·9	104	1·70
CD2TDS	6	368/9	139 (3)*	385 (3)	18·9	23·8	12·1	175	7·45
	6δ	300/3	133 (2)	374 (2)	—	—	—	178	5·19
	6ε	300/9	145 (2)	394 (2)	9·9	16·9	15·2	135	4·02

(*b*) Anharmonic-refinement results

Dataset name	No.	N/nv	α_{20}	β_{00}	DS	α_{33}	α_{40}	β_{20}	γ_{00}	R ($\times 10^4$)	σ
CD1TDS	2*b*	342/11	−0·5963	1·1179	2	0·017 (80)	0·130 (113)	−0·154 (147)	0·100 (105)	116	3·29
	2*f*	194/5			2	−0·189 (50)	0·187 (79)	−0·078 (148)	0·736 (117)	146	2·35
	2*g*	194/11			2	−0·041 (45)	0·164 (71)	−0·513 (126)	0·208 (101)	104	1·69
CD2TDS	6*b*	368/11	−0·6175	1·1429	6	0·023 (103)	0·288 (153)	−0·256 (174)	0·109 (112)	174	7·43
	6*f*	300/5			6	0·003 (64)	0·417 (931)	−0·718 (112)	0·514 (76)	175	5·09
	6*g*	300/11			6	−0·053 (56)	0·176 (88)	0·166 (131)	−0·252 (99)	131	3·94

* Replaces the erroneous value (0·0146) given in Rossmanith (1978).

correction obviously influences the results obtained for the temperature parameters as can be concluded from inspection of Table 3(*a*) as well as 3(*b*) by comparison of the results for the two samples.

The third-order parameter α_{33}, which rules the antisymmetric part of the thermal motion, is nonzero and negative for the special position $(\frac{1}{3}, \frac{2}{3}, \frac{3}{4})$ in Zn as well as in Cd. This result can reasonably be interpreted as enlargement of the amplitude of vibration in the basal plane of the hexagonal lattices of Zn and Cd in the direction towards the sides with rectangular holes between neighboring atoms and diminution in the opposite direction. The quantitative agreement between the α_{33} results of Merisalo & Larsen (1979) and the present work on Zn is poor, which again may be due to the different systematic errors involved and the lack of high-angle reflexions in both investigations.

In the case of Cd the anharmonic parameters were calculated in three steps for each sample. In the first step (datasets 2*b*, 6*b*) all reflexions were used. The resulting α_{33} value is positive for both samples. In the second step reflexions with high extinction correction ($y < 0{\cdot}9$) are removed from the datasets and the refinement is calculated using the remaining reflexions. The results of refinement on this data subset without extinction correction applied (2*f*, 6*f*) are not consistent. The refinements of the same datasets with extinction correction applied (2*g*, 6*g*) amount to fits with the smallest R and σ values and to similar values for α_{33}, but this value does not agree with that given by Merisalo, Peljo & Soininen (1978). The disagreement with the results of Field (1982) is possibly due to the different subsets of reflexions used in both analyses. The result for Cd given in this paper confirm Field's supposition that the anisotropic extinction correction applied to the whole data set masks the antisymmetric part of the thermal vibration.

In Table 5 the harmonic and anharmonic refinements are compared *via* Hamilton's ratio test, indicating a significant improvement of the fit for one Cd sample (CD2) only. In appraising this improvement one should have in mind the systematic errors obviously introduced into calculations by the various corrections and Hamilton's (1965) statement: 'All statistical tests demand the assumption of random errors in the data, and systematic errors can lead one to make gross errors in the application of hypothesis tests'. Therefore, the improvement of the fit may be due to the increased number of parameters only.

Having in mind the lack of improvement of the fit at least for sample CD1, and the discouraging inconsistency especially of the fourth-order anharmonic parameters one may question the usefulness of the anharmonic one-particle potential.

One reason why there is nevertheless interest in fourth-order anharmonic terms is the inadequacy of the harmonic approximation to account for the temperature variation of many physical properties of a crystal, for example the mean-square displacement of the atoms from their equilibrium position in a crystal. Therefore, one proof of the worth of anharmonic parameters is the test whether they result in mean-square displacements which suit the experimental data well for the whole temperature range.

Further investigation on more extensive datasets therefore seems valuable and necessary.

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Barium Diphosphate Tungsten Bronzes, $BaP_4O_8(WO_3)_{2m}$: X-ray Diffraction and High-Resolution Electron Microscopy Study

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(*Received* 30 *May* 1983; *accepted* 3 *January* 1984)

Abstract

A new series of diphosphate tungsten bronzes (DPTB's), $BaP_4O_8(WO_3)_{2m}$, has been prepared and investigated by X-ray diffraction and electron microscopy. Five pure members, $6 \leq m \leq 10$, have been characterized; calculated electron microscope images simulate experimental images and confirm that they belong to the DPTB family whose structure is built up from ReO_3-type slabs connected through P_2O_7 groups. Electron diffraction showed that the Ba DPTB's exhibit remarkable differences with respect to the alkaline bronzes: existence of an *A*-type lattice, presence of superstructure reflections and stability. Many samples, with integer and non-integer *m* values ($m \leq 20$), have been studied in order to determine the homogeneity and the defects occurring in the Ba DPTB's: many crystals are characterized by disordered intergrowths; however, several ordered intergrowths of the $m = 8$ and $m = 9$ members have been observed. The behaviour and the stability of these bronzes are discussed and compared to those of the alkaline DPTB's.

Introduction

The recent investigation of the *A*–P–W–O system has shown the existence of a new series of bronzes, $A_xP_4O_8(WO_3)_{2m}$ with $A = $ K, Rb, Tl (Giroult, Goreaud, Labbé & Raveau, 1980, 1981*a*, 1982, 1984; Labbé, Ouachee, Goreaud & Raveau, 1984; Hervieu & Raveau, 1982, 1983*a*, *b*). The host lattice of these compounds, called diphosphate tungsten bronzes (DPTB's), is built up from ReO_3-type slices connected through 'planes' of diphosphate groups forming hexagonal tunnels where the A^+ ions are located. For smaller ions such as Na^+ another tunnel structure is observed, $Na_xP_4O_8(WO_3)_{2m}$, called single phosphate tungsten bronzes (SPTB's) (Benmoussa, Groult, Labbé & Raveau, 1984); this latter structure is characterized by smaller but still hexagonal tunnels. This is to be compared to the A_xWO_3 bronzes of Magnéli (1949) which exhibit different tunnels according to the size of the A^+ ions. In this respect, the insertion of Ba^{2+} in such frameworks would be of interest since, in spite of its size being close to that of K^+, no Ba hexagonal tungsten bronze has been synthesized under atmospheric pressure; indeed, only tetragonal tungsten bronze Ba_xWO_3 ($0{\cdot}01 < x < 0{\cdot}33$) can be isolated (Conroy & Yokokawa, 1965; Ekström & Tilley, 1979). Moreover, the replacement of A^+ in these bronzes by Ba^{2+} could influence their electron-transport properties. Thus, the present work deals with the synthesis, X-ray diffraction and high-resolution electron microscopy (HREM) study of a new DPTB series, $BaP_4O_8(WO_3)_{2m}$.

0108-7681/84/030249-08$01.50