Canadian Mineralogist
Vol. 23, pp. 647-654 (1985)

ANHARMONIC THERMAL VIBRATIONS IN ZnO*

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ABSTRACT

A structural model of ZnO in the cumulant-expansion formalism has been studied with X-ray intensities measured on a spherical crystal at 293 and 473 K. In the least-squares refinements, the thermal vibrations appear isotropic for both atomic species at the two temperatures investigated. The equivalent isotropic temperature-factor B_{eq} of Zn varies from 0.581(2) to 0.892(5); that of O, from 0.577(9) to 0.829(19) Å^2. The only structural parameter, z of O, shows no significant change: 0.3821(1) at 293 K and 0.3820(2) at 473 K. At both temperatures, the measured amplitudes of reflections 35.*l* and 07.*l* (same *l*) are different: $|F(35.l)|$ is larger or smaller than $|F(07.l)|$ according as *l* is even or odd, while both reflections should have the same amplitude, on the assumption of spherical electron-density distributions, if the atoms vibrated with harmonic motions. The observed differences are interpreted with non-zero c_{111} for the third-order cumulant: c_{111} is positive for atoms at ⅓, ⅔, z and negative for atoms at ⅔, ⅓, ½ + z. Least-squares analyses of higher-order reflections give $c_{111} = 3.0(0.5) \times 10^{-5}$ for the 293 K data and $10.1(1.1) \times 10^{-5}$ for the 473 K data. The parameter c_{111} is directly compared with an effective potential one-particle parameter.

Keywords: ZnO (zincite), structure refined at 293 K and 473 K, cumulant-expansion formalism, thermal vibrations, anharmonic, different values of $|F(35.l)|$ and $|F(07.l)|$ at each temperature.

SOMMAIRE

Un modèle structural de ZnO a été étudié dans le formalisme d'expansion de cumulants au moyen d'intensités X diffractées, mesurées sur cristal sphérique à 293 et 473 K. Dans l'affinement par moindres carrés, les vibrations thermiques s'avèrent isotropes pour les deux espèces atomiques aux températures considérées. Le facteur de température isotrope équivalent de Zn varie de 0.581(2) à 0.892(5); celui de O, de 0.577(9) à 0.829(19) Å^2. L'unique paramètre structural, z de O, n'accuse par de changement significatif: 0.3821(1) à 293 K et 0.3820(2) at 473 K. Aux deux températures, les réflexions 35.*l* et 07.*l* (de même *l*) ont des amplitudes mesurées différentes: $|F(35.l)|$ est plus grand ou plus petit que $|F(07.l)|$ selon que *l* est pair ou impair, alors que, dans l'hypothèse d'une distribution sphérique de la densité électronique, les deux réflexions devraient avoir la même amplitude si les vibrations thermiques des atomes étaient harmoniques. On interprète les différences observées en considérant comme non-nul le c_{111} du cumulant de troisième ordre: c_{111} est positif pour les atomes à ⅓, ⅔, z et négatif pour les atomes à ⅔, ⅓, ½ + z. L'analyse aux moindres carrés des réflexions d'ordre élevé donne $c_{111} = 3.0(0.5) \times 10^{-5}$ pour les données à 293 K et $10.1(1.1) \times 10^{-5}$ pour les données à 473 K. Le paramètre c_{111} est directement comparable à un paramètre de potentiel effectif à particule unique.

Mots-clés: ZnO (zincite), structure affinée à 293 et 473 K, vibrations thermiques anharmoniques, valeurs différentes de $|F(35.l)|$ et $|F(07.l)|$ à chaque température.

INTRODUCTION

ZnO has the wurtzite-type structure, space group *P*6$_3$*mc*, in which both kinds of atoms are located in Wyckoff position 2*b* (⅓, ⅔, z) with site symmetry 3*m*. If atom Zn is fixed at $z = 0$, the number of positional variables reduces to one, namely z of atom O. In this structure, atoms of one kind are tetrahedrally co-ordinated by atoms of the other kind, with the two kinds of tetrahedra pointing in opposite directions. The term *tetrahedron* is used loosely to mean a trigonal pyramid (symmetry 3*m*). The trigonal pyramid of O about Zn points in the + **c** direction (Takeuchi 1977), which is readily identified by morphology: hexagonal pyramids terminate the + **c** end, whereas the negative direction − **c** is terminated by the large monohedron (000$\bar{2}$), which commonly is rounded.

In the structure one tetrahedral and three octahedral holes are found in the antibonding directions, along **c** and the $<\bar{1}.1.3(\frac{1}{2} - z)>$ vectors, respectively. The effective one-particle potential, O.P.P., around each atomic site, may well be anharmonic: the departure from harmonic (Gaussian) O.P.P. may result mainly from the antisymmetrical part represented by positive–negative lobes in the four bonding–antibonding directions. If the lobe along **c** differs from the other three, the atom would vibrate so that its mean position would be moved away from the position of minimum potential along the 3-fold axis (Mair & Barnea 1975, Mair & Wilkins 1981). The z parameter in ZnO, previously determined as 0.3826 (Sabine & Hogg 1969) and 0.3825 (Abrahams & Bernstein 1969), represents the mean position.

Mair & Barnea (1975) first presented a detailed

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*Paper presented at the XIIth I.U.Cr. Congress, Ottawa, 1981.

theoretical study of anharmonic thermal vibrations in wurtzite-type structures, using the O.P.P. and the generalized structure-factor expression of Dawson (1967). They also predicted that the origin of the primary pyroelectricity is related to the anharmonic thermal vibrations of the atoms, namely the separation between the position of minimum potential and the mean position. Based on similar structure-factor expressions, careful X-ray studies to determine anharmonic potential parameters of wurtzite-type compounds, CdS and CdSe, have been published by Whiteley *et al.* (1978) and by Fakineos *et al.* (1982), who have derived appropriate constraints, which reduce six anharmonic potential parameters to two, one for each atomic species, but these were also constrained as equal in the actual refinements.

In the present study of ZnO we have not followed their example but instead have used a model in the cumulant-expansion formalism of Johnson (1969, 1970) to determine the effect of anharmonic atomic vibrations on X-ray-structure amplitudes, and also accurately to determine the mean position and the probability-density function P.D.F. of O (or Zn) at 293 and 473 K. The position of minimum potential may be given as that of the mode of the P.D.F., but accurate determination of the P.D.F. was difficult, because of the high correlations between variables. A tentative position of the minimum of the potential is given in this study. Refinements were first carried out using all the observed reflections, and then using only high-order reflections so as to reduce bonding effects. Discussions are based on results from the high-order-reflections refinement.

EXPERIMENTAL

A transparent crystal from the International Monocrystal Co. was ground in a Bond grinder into a quasi-sphere, with its diameter ranging from 0.384 to 0.394 mm. Its X-ray intensities were measured at 293 and 473 K with Ag*Kα* radiation (λ = 0.5608 Å), monochromated by flat pyrolytic graphite on a Picker four-circle diffractometer. Intense reflections 00.2, 11.0 and 10.0 were examined at four different Ψ angles in a 90° range; no significant differences in intensity were observed, suggesting only minor anisotropic extinction. The + **c** direction was chosen, as previously done (Abrahams & Bernstein 1969), by comparing intensities of paired reflections 07.*l* and 35.*l* with the same *l* value (positive or negative), which occur at the same 2θ angle. Intensities of reflections within one quadrant (for the 293 K data) and within a hemisphere (for the 473 K data) were measured for *l* positive in the θ–2θ scan mode and in a range of $(\sin\theta)/\lambda$ up to 1.5 Å^{-1}. They were converted to structure factors after being corrected for Lorentz, polarization and absorption effects. Agreement in the $|F_o|$ for equivalent reflections is sufficiently good for the 293 K data. The average of $\Sigma \,\|F_j| - <|F|>\| / \Sigma|F_j|$ was only 1.4 % for 247 sets of symmetry-related reflections. This average changes to 2.3% for 227 sets of the 473 K data; temperature variations as large as ±5 K could not be prevented. Nevertheless we decided to try least-squares refinements at both temperatures. The averaged amplitudes were corrected for one-phonon TDS (thermal diffuse scattering) with the correction factors based on the program *SXTDS*–1 (Kurittu & Merisalo 1977), which was written for the method of Merisalo & Kurittu (1978). Elastic constants were taken from Slobodnik *et al.* (1973) and Tokarev *et al.* (1975). The effect of the TDS is largest in the **c** direction, but its anisotropy is very small: the maximum value of the correction factors was 19.7% for the 293 K data and 22.6% for the 473 K data at $\sin\theta/\lambda \simeq 1.44$ Å^{-1}.

Cell constants were measured at seven temperatures from 293 to 623 K, on a second, smaller, spherical crystal mounted on a Philips PW 1100 four-circle diffractometer. Mo*Kα* radiation (λ = 0.71069 Å), monochromated with pyrolytic graphite, was used to measure the centroids of profiles for twelve reflections at each temperature. Each reflection was measured twice, at positive and negative 2θ positions so that twenty-four observations were available to fit the cell dimensions in least-squares calculations at each temperature (Table 1). The cell dimensions used for crystal #1, in the calculations below, were taken from the two lines of best fit obtained for these data (Table 1).

A very small decrease in axial ratio with increasing temperature is observed, as was explained by Mair & Barnea (1975). The slope of the line of best fit for *c/a versus* T (Fig. 1) is very similar to that obtained for Khan's (1968) data, but the present *c* values are seen to be smaller (Table 1) than his and those of Abrahams & Bernstein (1969) (Table 6). Our synthetic sample was not analyzed for chemical purity and may contain a very small amount of ions other than Zn. Since our study deals with the ther-

TABLE 1. CELL CONSTANTS, c/a RATIO AND CELL VOLUME FUNCTIONS OF TEMPERATURE

T(K)	a(Å)	c(Å)	c/a	V(Å^3)	F.R.**
293	3.2494(9)	5.2038(14)	1.6015(7)	47.584	0.9872
300*	3.2500(1)	5.2078(4)	1.6022(2)		
373	3.2514(3)	5.2050(9)	1.6009(4)	47.653	0.9869
443	3.2522(4)	5.2067(11)	1.6010(4)	47.692	0.9870
463	3.2532(2)	5.2072(6)	1.6006(3)	47.726	0.9868
(473	3.2533(5)	5.2073(13)	1.6006(6)	47.730	0.9868)
493	3.2536(5)	5.2076(12)	1.6006(5)	47.742	0.9867
498*	3.2540(1)	5.2108(5)	1.6014(2)		
523	3.2543(2)	5.2082(6)	1.6004(3)	47.768	0.9867
622*	3.2569(1)	5.2141(4)	1.6009(2)		
623	3.2563(8)	5.2112(17)	1.6003(7)	47.854	0.9867

* Values taken from Khan (1968). ** F.R. = $(a^2/3 + c^2/4)^{1/2}/a$ = flatness ratio for co-ordination polyhedron = (edge inclined to c)/(edge perpendicular to c). Lines of best fit for present data: $a = 3.24343 + 2.068 \times 10^{-5}$ T (Å) and $c = 5.19692 + 2.219 \times 10^{-5}$ T (Å).

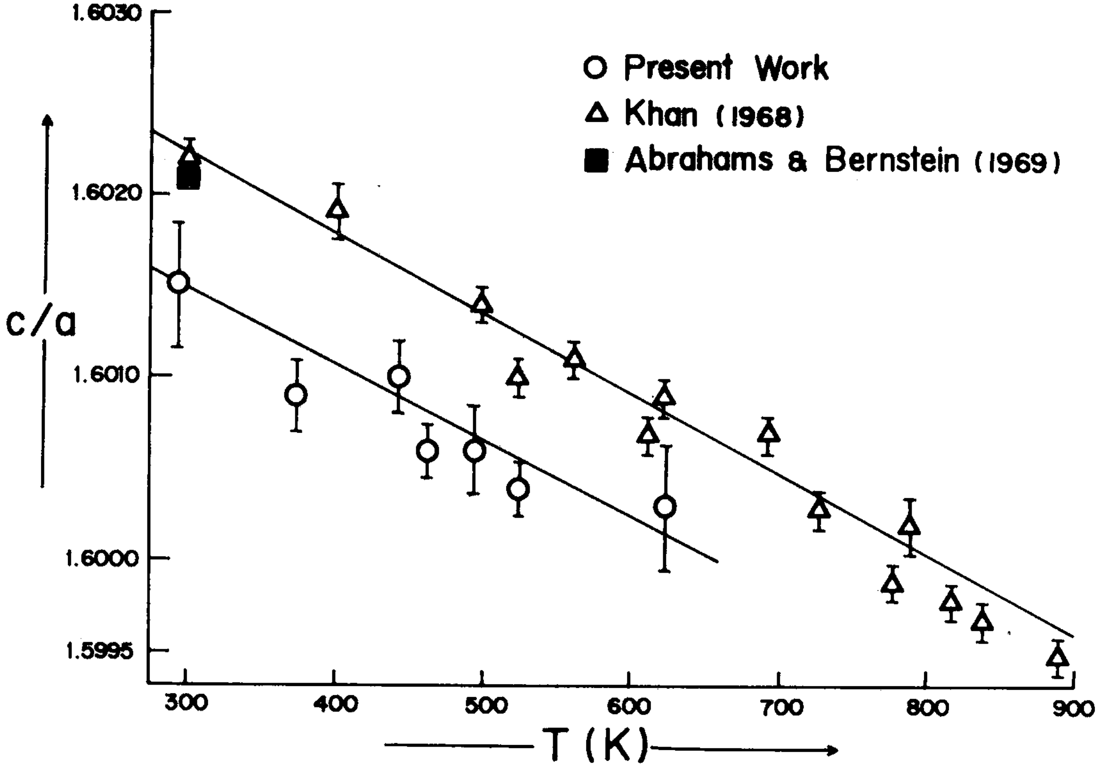

FIG. 1. Axial ratio c/a *versus* temperature T.

mal behavior of a mineral species that commonly shows solid solution (limited substitution of Mg, Co, Mn^{2+} and Fe^{2+} for Zn) and a wide range of cell dimensions (V 46.51 to 48.16 Å^3) (Crystal Data, 1973), we are not concerned about the above discrepancy. Our cell dimensions give coefficients of linear expansion of 6.4×10^{-6}/K along **a** and 4.3×10^{-6}/K along **c**, at 293 K.

OBSERVATIONS OF ANHARMONIC THERMAL VIBRATIONS

In wurtzite-type compounds, reflections $hk.l$ with $h-k = 3n$(n: integer) are extinct if l is odd, provided spherical scattering factors are assumed and atomic thermal vibrations are harmonic. Let us write the expression for the structure factor that includes up to third-order cumulant terms

$$F(\mathbf{h}) = \sum_{j=1}^{2} G_j(\mathbf{h})\, H_j(\mathbf{h}), \qquad (1)$$

where we have:

$$G_j(\mathbf{h}) = f_j(\mathbf{h}) \exp[-b_j^{11}q - b_j^{33}l^2] \exp[-i(3c_j^{113}\, ql + c_j^{333}l^3)] \exp[2\pi i l z_j]$$

with $q = h^2 + hk + k^2$

and

$$H_j(\mathbf{h}) = \{\exp[2\pi i(h-k)/3]\exp[-ic_j^{111}\, p] + (-1)^l\exp[-2\pi i(h-k)/3]\exp[ic_j^{111}\, p]\}$$

with $p = h^3 - k^3 + (3/2)hk(h-k)$.

The atomic scattering factor has the usual form

$$f(\mathbf{h}) = f_0 + f' + if''.$$

In equation (1), j refers to Zn and O at ⅓, ⅔, z. The three independent coefficients of the third-order terms are c^{111} $(= -c^{222} = 2c^{112} = -2c^{122})$, c^{333} and c^{113} $(= c^{223} = 2c^{123})$ for all the atoms in ZnO.

For c^{111} values other than zero and $p \neq 0$ ($h \neq k$, $-k/2$, $-2k$), the above extinction-rule, due to atoms in the $2b$ Wyckoff position, is not obeyed since

$$F(\mathbf{h}) = -2i \sum_{j=1}^{2} G_j(\mathbf{h}) \sin(c_j^{111} p). \qquad (2)$$

Intensities of such reflections were too weak to be considered significantly different from zero.

There occur two series of reflections at high Bragg angles, which have identical values of q but different values of p; they are 35.l and 07.l and their symmetry-equivalent reflections. Using a temperature-factor expression based on the O.P.P. functions written in the form of cubic harmonics, Whiteley *et al.* (1978) showed that the two sets of reflections with the same l can have different amplitudes in the anharmonic model, whereas in the harmonic one they must have the same amplitudes. They reported X-ray-intensity differences between 07.l and 35.l, which they obtained from a large crystal of CdSe.

From the same observed structure-factors of ZnO, namely 35.l and 07.l, averaged over their (twelve or six) equivalent reflections, and their estimated standard deviations (Table 2), it can be seen that the amplitudes of the 35.l reflections tend to be larger than those of the 07.l reflections if l is even, and smaller if l is odd, although, at the one-sigma level, the two amplitudes are equal in six cases out of nine. The intensity, $I = FF^*$, of a reflection can be written as follows:

$$\begin{aligned} I = {} & 2G_{\mathrm{Zn}}G^*_{\mathrm{Zn}}\{1 + (-1)^l\cos[2\pi(h-k)/3 + 2c_{\mathrm{Zn}}{}^{111}p]\} \\ & + 2G_{\mathrm{O}}G^*_{\mathrm{O}}\{1 + (-1)^l\cos[2\pi(h-k)/3 + 2c_{\mathrm{O}}{}^{111}p]\} \\ & + 2(G^*_{\mathrm{Zn}}G_{\mathrm{O}} + G_{\mathrm{Zn}}G^*_{\mathrm{O}})\{\cos[(c_{\mathrm{O}}{}^{111} - c_{\mathrm{Zn}}{}^{111})p] + \\ & (-1)^l\cos[2\pi(h-k)/3 + p(c_{\mathrm{Zn}}{}^{111} + c_{\mathrm{O}}{}^{111})]\}. \end{aligned} \qquad (3)$$

The observed intensity-relations (Table 2) warrant the conclusion that the c^{111} value must be positive, and non-zero, as shown by (3).

TABLE 2. STRUCTURE AMPLITUDES OF REFLECTIONS 35.ℓ AND 07.ℓ AND THEIR E.S.D. AT 293 K

$h\ k\ \ell$	$\lvert Fo\rvert$	$\lvert Fc\rvert$	$\sigma\lvert Fo\rvert$	$h\ k\ \ell$	$\lvert Fo\rvert$	$\lvert Fc\rvert$	$\sigma\lvert Fo\rvert$	$\Delta\lvert Fo\rvert$	$\Delta\lvert Fc\rvert$
3 5 0	3.21	3.21	0.08	0 7 0	3.09	3.13	0.03	0.12	0.08
3 5 1	4.12	4.15	0.11	0 7 1	4.17	4.19	0.10	-0.05	-0.04
3 5 2	2.72	2.66	0.14	0 7 2	2.61	2.60	0.09	0.11	0.06
3 5 3	4.94	4.96	0.06	0 7 3	4.93	5.00	0.15	0.01	-0.04
3 5 4	2.06	1.99	0.19	0 7 4	1.96	1.94	0.04	0.10	0.05
3 5 5	4.45	4.44	0.16	0 7 5	4.50	4.48	0.07	-0.05	-0.04
3 5 6	2.25	2.09	0.06	0 7 6	2.08	2.04	0.06	0.17	0.05
3 5 7	3.07	2.97	0.10	0 7 7	3.08	2.99	0.08	-0.01	-0.02
3 5 8	1.98	2.00	0.07	0 7 8	1.80	1.95	0.14	0.18	0.05

$\Delta\lvert Fo\rvert$ and $\Delta\lvert Fc\rvert^*$ are taken as $\lvert F_{35.\ell}\rvert - \lvert F_{07.\ell}\rvert$. * Calculated with numerical values obtained from high-order-reflections refinement of model based on 3-c formalism.

REFINEMENT WITH THE CUMULANT-EXPANSION FORMALISM

Refinements of structure models with second- and third-order cumulant-expansion terms (abbreviated 2-c and 3-c), at 293 and 473 K, were initiated with all the observed amplitudes, and then repeated with amplitudes of high-order reflections only, in attempts to reduce bonding effects. The numbers of reflections used, at 293 and 473 K, are 247 and 227 for the all-data refinements, and 181 and 163 for the high-order-reflections refinements, respectively. The least-squares program *ORXFLS4* (Johnson 1969), which is in the 1977 version of *ORFLS* (Busing *et al.* 1962), was used. The 2-c calculation includes the z co-ordinate of oxygen and the four atomic temperature-factors b^{ij}; the model obtained from 3-c requires six more third-order terms c^{ijk} (three for each atomic species). In addition, a scale factor and an isotropic extinction factor were included in the least-squares refinements. Weighting schemes were based on the expression

$$w^{-1} = 1/(N-1)\Sigma(|F_j| - <|F|>)^2, \qquad (4)$$

where summation is over N equivalent reflections, and the carets indicate taking an averaged value of the equivalent reflections. Spherical atomic scattering-factors and correction terms for anomalous dispersion were taken from the tables of Cromer & Waber, and of Cromer, respectively, in the *International Tables for X-ray Crystallography,* vol. IV (1974).

The terms c^{333} and c^{113} can express the skewness of P.D.F., which is symmetrical around the three-fold axis but antisymmetrical in the plane passed through the mean of the P.D.F. perpendicularly to the three-fold axis: positively and negatively maximized in the bonding–antibonding direction in the three-fold axis. In addition, c^{113} can also show the skewness that is maximized (positively and negatively) in a cone surface radiating from the mean of the P.D.F. to include the remaining three bonding–antibonding directions. The terms c^{113} and c^{333}, and even z, are strongly correlated. Bonding effects will also influence c^{113} and c^{333}. On the other hand, c^{111} is not directly correlated with the bonding–antibonding directions. Skewness expressed by c^{111} is antisymmetrical around the three-fold axis, but symmetrical in the plane passed perpendicularly to the three-fold axis through the mean of the P.D.F., where positive and negative lobes of skewness-contours lie. The term c^{111} obtained in the least-squares refinements should be less affected by other terms and bonding electron-density distribution.

The terms c^{113}, c^{333} and z in the model obtained from 3-c show a strong corrrelation; it was impossible to determine these terms independently in the least-squares refinements.

Refinements based on all the data

Lists of parameters, information on "all-data" refinements, and 3-c structure factors of high-order reflections are available at nominal cost from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

The refinements of the model obtained from 2-c converged to weighted R values, R_w, of 1.23 and 2.29%, and z values of 0.3817(1) and 0.3817(2), for the 293 and 473 K data, respectively. The second-order terms, b^{ij}, are very nearly equal for the two kinds of atom, strongly suggesting that the difference between atomic masses is irrelevant for these terms, and that the P.D.F. values for the two kinds of atom are very nearly equal. From consideration of 'chemical antisymmetry' (black–white groups) in ZnO, where an antimirror m', perpendicular to the three-fold axis at $z' = z/2$, interchanges cations and anions, we can assume that the P.D.F. for the two kinds of atoms are skewed antisymmetrically about m'.

The third-order terms c^{113} and c^{333} occur only as differences between the two kinds of atoms, $c_O{}^{113} - c_{Zn}{}^{113}$ and $c_O{}^{333} - c_{Zn}{}^{333}$ in the intensity expression (3), implying that neither term is uniquely determined for either atom. In an attempt to refine all parameters simultaneously in the model obtained from 3-c, c^{113} and c^{333} for both Zn and O were constrained by the program so that $c_O{}^{113} = -c_{Zn}{}^{113}$ and $c_O{}^{333} = -c_{Zn}{}^{333}$. This combination of constraints is also a consequence of the assumed antisymmetrical P.D.F. for each kind of atom. In the following calculations, several possible combinations of constraints were examined, but a set of constraints $c_O{}^{113} = -c_{Zn}{}^{113}$, $c_O{}^{333} = -c_{Zn}{}^{113}$ and $c_O{}^{111} = c_{Zn}{}^{111}$ was accepted as the best, because the number of constraints in it is the minimum compatible with reasonable e.s.d. values for the third-order coefficients.

The model obtained from 3-c with the constraints given above was refined to R_w of 1.15 and 2.14%, and z of 0.3809(3) and 0.3803(7), for the 293 and 473 K data, respectively. For the 293 K data, c^{111} and c^{333} were refined to values significantly different from zero. The correlations between c^{111} and other remaining terms are lower than 0.25, whereas those between c^{113} and c^{333}, c^{333} and z, and c^{113} and z are strong: the maximum value is 0.85 between z and c^{333}. Only for the 473 K refinement is c^{111} significantly different from zero. The largest extinction, $|F_o|^2/|F_c|^2$, is 0.35, observed for 00.2.

TABLE 3. POSITIONAL AND THERMAL PARAMETERS IN MODELS REFINED IN 2-c AND 3-c USING HIGH-ORDER REFLECTIONS ONLY AT 293 AND 473 K

2-c	z	b^{11}	b^{33}			
			293 K*			
O	0.3821(1)	0.0181(2)	0.0054(2)			
Zn	0.0	0.0182(1)	0.0054(1)			
	R = 0.0102, R_w = 0.0107 and S = 1.0538					
			473 K**			
O	0.3820(2)	0.0261(6)	0.0076(2)			
Zn	0.0	0.0280(2)	0.0083(1)			
	R = 0.0185, R_w = 0.0205 and S = 0.8266					
3-c	z	b^{11}	b^{33}	c^{111}	c^{333}	c^{113}
			293 K*			
O	0.3830(4)	0.0182(2)	0.0054(1)	3.0	2.7	1.7
Zn	0.0	0.0183(1)	0.0054(1)	3.0(0.5)	-2.7(1.5)	-1.7(1.9)
	R = 0.010, R_w = 0.0095 and S = 0.944					
			473 K*			
O	0.3778(5)	0.0259(5)	0.0074(2)	10.1	-8.1	-9.7
Zn	0.0	0.0278(2)	0.0082(1)	10.1(1.1)	8.1(2.3)	9.7(2.1)
	R = 0.0158, R_w = 0.0157 and S = 0.639					

* 181 reflections, ** 163 reflections.
Values of $(\sin\theta)/\lambda$ of reflections used are larger than 0.9 Å^{-1}.
Values of c^{ijk} are multiplied by 10^5.

TABLE 4. MEAN-SQUARE-DISPLACEMENTS, $\langle u^2\rangle$, PARALLEL AND PERPENDICULAR TO c AT 293 AND 473 K*

	293 K		473 K	
	⊥ c axis	‖ c axis	⊥ c axis	‖ c axis
Zn	0.00731(03)	0.00745(05)	0.01128(08)	0.01134(09)
O	0.00725(13)	0.00743(23)	0.01050(30)	0.01050(40)

* 2-c refinements based on high-order reflections only.

Refinements based on high-order reflections only

The z value and thermal tensor coefficients, obtained from the data set with the lower limit of $(\sin\theta)/\lambda$ of 0.9 Å^{-1}, are listed for both 293 and 473 K data (Tables 3, 4), together with R values and 'goodness of fit' S. Extinction corrections were found to be negligibly small for all high-order reflections.

The high-order-reflections refinements of the model obtained from 2-c converged to z of 0.3821(1) and 0.3820(2), and R_w of 1.07 and 2.05% for the 293 and 473 K data, respectively (Table 3).

The same constraints as in the "all-data" refinement of the model from 3-c were applied to the least-squares calculations of high-order reflections. Seven limiting values of $(\sin\theta)/\lambda$, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1 and 1.2 Å^{-1}, were applied to exclude low-order reflections. The case for 0.9 Å^{-1} was chosen as representative of this refinement, because using reflections above 0.9 Å^{-1} led to similar values for each parameter in 2-c and 3-c.

The positional parameter z in the refinements

TABLE 5. INTERATOMIC DISTANCES AND ANGLES OBTAINED* AT 293 AND 473 K

	293 K	473 K	Δ(473-293)
Zn - O (apical) (Å)	1.9884(8)	1.9892(9)	0.0008(12)
3 × Zn - O (basal) (Å)	1.9738(4)	1.9762(6)	0.0024(8)
(Å)	0.0142	0.0127	-0.0015
O - Zn - O (apical)	108.12(2)°	108.12(3)°	0.00°
O - Zn - O (basal)	110.79(2)°	110.79(3)°	0.00°

* 2-c refinements based on high-order reflections only.

TABLE 6. PAST AND PRESENT PERTINENT CRYSTALLOGRAPHIC DATA ON ZnO

Crystal data: $P6_3mc$, Z = 2, wurtzite-type structure, ideal value c/a = 1.633, z(O) = 0.375 for regular coordination-tetrahedron.

References	present*	present*	S & H†	A & B‡
Temperature	293 K	473 K	-	298 K
a (Å)	3.2494(9)	3.2533(5)	3.2427	3.249858(6)
c (Å)	5.2038(14)	5.2073(13)	5.1948	5.206619(2)
c/a	1.6015	1.6006	1.6020	1.6021
z(O) 2-c	0.3821(1)	0.3820(2)	0.3826(7)	0.3825(14)
B^{eq}(Zn) (Å^2)	0.567(2)	0.931(5)	0.550(80)	0.630(20)
B^{eq}(O) (Å^2)	0.572(9)	0.866(19)	0.310(60)	0.680(70)
Debye temperature	387 K	393 K	-	370 K
Wavelength (Å)	0.5608(AgKα)		1.09 (neutrons)	0.7107(MoKα)
No. of obs. refl.	181	163	33	141 used, but only 121 symmetry-independent ones
Extinction corrections:	isotropic	isotropic	-	isotropic
TDS correction:	applied	applied	-	-
Absorption correction:	applied to spherical crystal		-	applied to spherical crystal
R 2-c	0.0102	0.0185	0.047	0.0378
3-c	0.0100	0.0158	-	-
R weighted				
2-c	0.0107	0.0205	-	0.0512
3-c	0.0095	0.0157	-	-
Goodness of fit, S				
2-c	1.054	0.827	-	0.861
3-c	0.944	0.639	-	-

* Values, except cell constants, are from refinements based on high-order reflections. † Sabine & Hogg (1969), ‡ Abrahams & Bernstein (1969).

based on 2-c of the 293 K and 473 K data changed respectively from 0.3817(1) and 0.3817(2), for all the reflections, to 0.3821(1) and 0.3820(2), for the high-order reflections only. The values of c^{111} slightly increased from 2.7(6) to 3.0(5) × 10^{-5}, and 9.9(1.8) to 10.1(1.1) × 10^{-5}, for the 293 and 473 K data, respectively. These differences between refinements are smaller than the corresponding (one-) sigma values. In the present study, we take the values obtained from the high-order reflections, since, in their intensities, extinction effects are negligible, and contribution from bonding electrons is considered to be small.

The values of z and b^{ij} taken from Table 3 (2-c formalism) can be considered unbiased estimates of the mean and the dispersion, respectively, of the P.D.F. (Johnson 1969, 1970). The z values obtained in the 3-c refinements should be disregarded, even if they were free from correlations, because they are biased by the neglect of higher odd-order terms. Interatomic distances and angles for the means of the atomic P.D.F. are shown (Table 5), and a summary of pertinent crystallographic data of past and present refinements of the structure of ZnO is presented (Table 6) to facilitate comparisons.

DISCUSSION

There is no significant change in z (the mean of P.D.F.) with temperature, whereas the change of c/a in the same range of temperature equals about two e.s.d. but is definitely part of a trend: c/a decreases with increasing temperature (Table 1). Let us compare our results with the two predictions offered by Keffer & Portis (1957), who assumed that departures of wurtzite-type structures from the ideal c/a value could be related to z as a function of nearest-neighbor bond-bending as follows: $z = \frac{1}{2} - (1/24)^{\frac{1}{2}}(a/c)$. For bond-stretching as the major cause of the deviation from the ideal c/a value, they offer the relation: $z = \frac{1}{4} + (\frac{1}{3})(a/c)^2$. With our a/c values 1/1.6015 and 1/1.6006 for temperatures of 293 and 473 K (Table 1), these two equations give $z = 0.3725$ at both temperatures for the bond-bending relation and z equal to 0.3800 and 0.3801 for the bond-stretching relation. The experimentally determined z value, the same at both temperatures within the accuracy of the determination, is 0.3821(1) or 0.3820(2) (Table 3), significantly above the highest predicted value. This result is in agreement with the conclusion reached by Mair & Barnea (1975), who stated that the two relations given above underestimate the observed z value, but that the bond-stretching relation comes closer to the experimental value than the bond-bending relation.

The numerical values of b^{ij} were little affected by the introduction of the third-order terms. The harmonic thermal vibrations of the atoms appear almost isotropic, being slightly preferred along the 3-fold axis (Table 5): the equivalent isotropic temperature-factor B_{eq} of Zn varies with temperature from 0.581(2) to 0.892(5), whereas that of O varies from 0.577(9) to 0.829(19) Å^2. These values give Debye temperatures of 387 and 393 K from the data obtained at 293 and 473 K, respectively, where $B = (6h^2T/mk_B\Theta^2)[\phi(x) + (\frac{1}{4})x]$ (see, for example, Willis & Pryor 1975); m is taken as the average mass of Zn and O. A lower value of 370 K (Table 6) was obtained by Abrahams & Bernstein (1969).

The shape of the trigonal pyramid of atoms of one kind about an atom of the other kind changes slightly with temperature (Table 1). The Zn–O distance inclined to c increases more than that parallel to c when the temperature is raised from 293 to 473 K, and the angle O–Zn–O remains constant (Table 5).

The third-order-cumulant term, $c^{111} = 3.0(0.5) \times$

10^{-5}, obtained from the high-order-reflections refinement at 293 K is compared with the "potential parameter" β_1 of Mair & Barnea (1975). In their O.P.P. model, β_1 is the coefficient of one of the three cubic terms that represent the O.P.P. in the directions perpendicular to the three-fold axis. It is related to c^{111} as follows:

$$\beta_1 = 27a^3\alpha_1{}^3c^{111}/(128\pi^3k_B{}^2T^2) \qquad (5)$$

where α_1 is given by $\alpha_1 = k_BT/<u_1{}^2>$. With our 293 K data the potential parameter β_1, calculated from equation (5), has the value 0.73×10^{-12} (erg Å^{-3}).

In a P.D.F. map (extended Edgeworth expansion) computed for the cumulants obtained from the high-order-reflections refinements of the 293 K data (Table 3), the peak position, which we interpret as the position of minimum potential, is located at $z = 0.3797$, in agreement with that predicted by Mair & Barnea (1975). However, the strong correlations between the odd-order tensors, except c^{111}, prevent us from drawing any conclusion about the details of the P.D.F., and this value should be regarded as tentative until we can find a solution free from the correlation problem.

ACKNOWLEDGEMENTS

We are grateful to Dr. S. Mair for reading an early version of the manuscript and suggesting corrections. We also thank Prof. M.J. Merisalo for sending us the computer program SXTDS-1, Dr. T. Yamanaka, who read the manuscript, and Professor B.W. Batterman, who kindly gave us time of the Chess synchrotron at Cornell University, where K.K. tried, unsuccessfully, to obtain more X-ray intensities for improving the refinement. Professor Emeritus J.D.H. Donnay helped prepare the final text, and Mr. K. Nakamura drew the figure. K. K. thanks the Faculty of the Department of Earth Sciences at Kanazawa University for supporting his leave of absence, and G.D. thanks them for their hospitality during her stay at their Institution. Thanks are also due to the referees and the former co-editor, Dr. F.R. Ahmed of *Acta Crystallographica,* who first processed this paper, had accepted it, but graciously released it to *The Canadian Mineralogist*. Last, but not least, we thank Ms. Noriko Kihara for the full-time assistance during the Cornell episode.

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Submitted for publication August 7, 1984, revised manuscript accepted April 15, 1985.