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On Antisymmetric Atomic Vibrations in Zinc

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Abstract

Recent elastic neutron scattering data [Merisalo & Larsen (1977). *Acta Cryst.* A**33**, 351–354] have been reconsidered. A significant value for the cubic anharmonic force constant $\alpha_{33} = -1{\cdot}80\,(30) \times 10^{-19}$ J Å^{-3} of the one-particle potential was obtained, and is compared with other recent determinations.

In a previous paper (Merisalo & Larsen, 1977; hereinafter referred to as paper I) we reported the results and analysis of a neutron single-crystal diffraction study of Zn at 300 K. The data, interpreted in the framework of the effective one-particle potential approximation, showed significant quartic terms in the anharmonic potential, whereas the value of the cubic (antisymmetric) anharmonic parameter α_{33} representing deviations from axial symmetry in the initial analysis did not differ significantly from zero and was consequently ignored in the final refinement.

Recently, a non-zero value for α_{33} was determined by an X-ray measurement of almost-forbidden reflexions 301 and 303 (Merisalo, Järvinen & Kurittu, 1978). It was therefore considered desirable to reassess the validity of the assumption $\alpha_{33} = 0$ made in our neutron data analysis. In this paper we shall also discuss correlations between the various parameters and describe qualitatively the atomic thermal motion in the anharmonic approximation.

Each unit cell of h.c.p. Zn contains two atoms, *A* and *B*, at the special positions $\pm(\frac{1}{3},\frac{2}{3},\frac{1}{4})$. The origin, taken midway between these two points, is an inversion centre. A basal projection of the atomic arrangement and the definition of the atomic Cartesian coordinate system *xyz* (*x* axis along 2, *y* axis perpendicular to *m*, *z*-axis along $\bar{6}$) is shown in Fig. 1. The exact expression for the structure amplitudes $F(\mathbf{Q})$ becomes

$$F(\mathbf{Q}) = 2b\left[T_{s,A}(\mathbf{Q})\cos 2\pi\left(\frac{h+2k}{3}+\frac{l}{4}\right) - T_{a,A}(\mathbf{Q})\sin 2\pi\left(\frac{h+2k}{3}+\frac{l}{4}\right)\right],$$

where $T_{s,A}(\mathbf{Q})$ and $T_{a,A}(\mathbf{Q})$ are the symmetric and antisymmetric (*i.e.* real and imaginary) parts of the atomic temperature factor $T(\mathbf{Q})$ given in paper I, $\mathbf{Q}$ is the diffraction vector, and b is the scattering length. This expression was used for the calculated structure amplitudes in refining the potential parameters by a least-squares method. Refinements were made applying model 2 of paper I in which the harmonic parameters were kept fixed at the values determined from the

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theoretical calculation of Barron & Munn (1967), this model having been concluded to constitute an appropriate model for discussion of intrinsic anharmonic effects.

As a first stage, we repeated the refinement of the quartic anharmonic parameters by fixing $\alpha_{33} = 0$ (model 2 of paper I), and by using a revised version of the least-squares program implying a slightly different estimate for the standard deviation of the variable parameters. The results of this refinement are given in Table 1, column 2. We note that the value of the isotropic fourth order parameter γ_{00} remains unchanged, whereas the values of α_{40} and β_{20}, which are strongly correlated, differ to some extent from the values given in paper I. In order to discuss the significance of these differences, we recall our earlier conclusion concerning the problems arising from strong correlations. This is that the anharmonic effects can be discussed more conveniently by studying some integral parameters characterizing the thermal smearing function as a whole rather than the individual values of strongly correlated anharmonic parameters separately. Such integral quantities are, for example, the second moments of the atomic displacements (*i.e.* the mean-square displacements of atomic vibrations), which at the high-temperature limit can be evaluated from the Boltzmann distribution function. Their values in the principal directions, given in Table 1, are practically identical to those arrived at in paper I, which implies that the alterations in the individual values of α_{40} and β_{20} are of no consequence.

Table 1. *Refinements for Zn with anharmonic temperature factor $T(\mathbf{Q})$*

$\langle u_x^2 \rangle$ and $\langle u_z^2 \rangle$ are the second moments of atomic displacements (or the mean-square displacements) and $R_w = \sum w||F_o| - |F_c||/\sum w|F_o|$. E.s.d.'s are given in parentheses and refer to the final digits. The number of reflexions was 32.

	Model 2	Model 3	
α_{20}	−1·109 (10)	−1·109 (10)	$\times 10^{-19}$ J Å^{-2}
β_{00}	1·841 (10)	1·841 (10)	$\times 10^{-19}$ J Å^{-2}
α_{33}	–	−1·80 (30)	$\times 10^{-19}$ J Å^{-3}
α_{40}	0·08 (27)	0·25 (28)	$\times 10^{-19}$ J Å^{-4}
β_{20}	7·27 (28)	7·36 (28)	$\times 10^{-19}$ J Å^{-4}
γ_{00}	−6·11 (14)	−6·27 (14)	$\times 10^{-19}$ J Å^{-4}
R_w	0·0128	0·0115	–
$\langle u_x^2 \rangle$	0·0113 (3)	0·0113 (3)	Å^2
$\langle u_z^2 \rangle$	0·0259 (5)	0·0258 (5)	Å^2

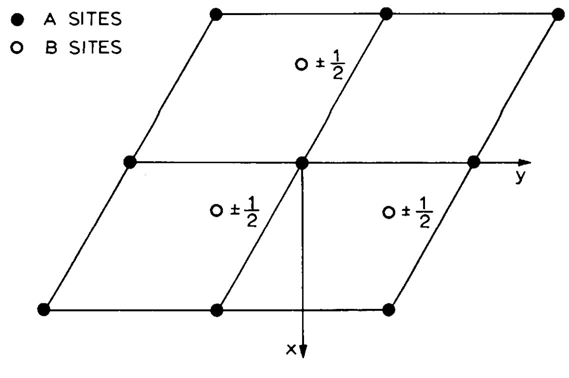


Fig. 1. A basal projection of the atomic arrangement of Zn and the definition of the atomic Cartesian coordinate system *xyz*.

In the second stage, the third order parameter α_{33} was varied together with the fourth order parameters. The results of this refinement are listed in Table 1, column 3 (model 3), and the corresponding least-squares correlation matrix is given in Table 2. We note that the cubic anharmonic parameter α_{33} is only weakly correlated with the quartic anharmonic parameters and, correspondingly, that the values of the latter as well as the values of the second moments of the atomic displacements (in which the contribution of α_{33} is identically zero) are essentially equal to those of model 2. Thus it can be concluded that the present value of $\alpha_{33} = -1{\cdot}80\,(30) \times 10^{-19}$ J Å^{-3} represents a direct manifestation of the third order intrinsic anharmonic effects in Zn.

A non-zero value of α_{33} implies axial anisotropy about the hexagonal axis. This agrees with measurements of the hydrostatic and uniaxial stress dependence of ultrasonic velocity which show slightly different values for the third order elastic constants C_{111} and C_{222} (Swartz & Elbaum, 1970). The present result is also in accord with the value $-1{\cdot}83 \times 10^{-19}$ J Å^{-3} estimated from thermal expansion data (Nizzoli, 1978), and with the value $-1{\cdot}5\,(3) \times 10^{-19}$ J Å^{-3} determined from an X-ray measurement of the almost forbidden reflexions 301 and 303 (Merisalo, Järvinen & Kurittu, 1978).

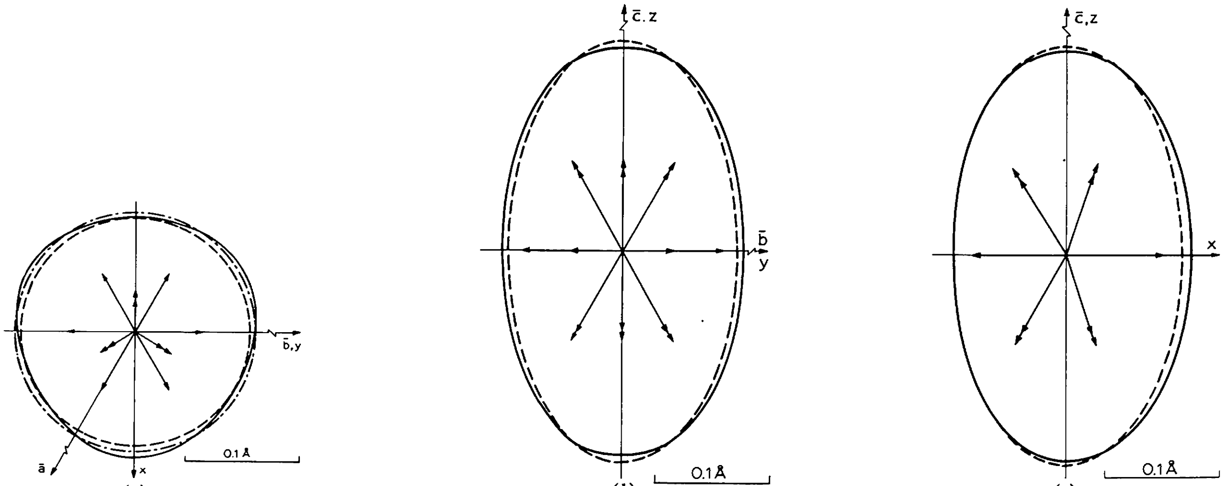
The other conclusions presented in paper I remain valid, as is verified by the identical values of the second moments which best describe the fourth order anharmonic effects.

A qualitative description of the atomic thermal motion in the anharmonic approximation can be obtained by plotting equipotential contours in a set of planes through an atom.

Equipotential contours $[V(u) = 0{\cdot}025 \times 10^{-19}\ \mathrm{J}]$ in the basal plane are plotted in Fig. 2(*a*) and illustrate the symmetric and antisymmetric distortions of the effective one-particle potential function due to anharmonic terms. The potential is softened in the $+x$ direction and hardened in the opposite direction, which indicates larger amplitudes of vibration towards the side with rectangular holes between neighbouring atoms than towards the side with triangular holes.

Table 2. *Least-squares correlation matrix for the refinement in the framework of model* 3

	α_{33}	α_{40}	β_{20}	γ_{00}
α_{33}	1·000			
α_{40}	0·093	1·000		
β_{20}	0·064	0·845	1·000	
γ_{00}	0·199	0·467	0·865	1·000



(a) (b) (c)

Fig. 2. Equipotential contours [$V(\mathbf{u}) = 0{\cdot}025 \times 10^{-19}$ J] in Zn, (*a*) in the basal plane, (*b*) in *yz* plane (plane perpendicular to a mirror plane), (*c*) in *xz* plane (a mirror plane). Arrows with one tip are the direction indicators or their projections of the nearest neighbours, arrows with two tips are those of the next-nearest neighbours (*cf.* Fig. 1). Dashed lines are obtained by including only the harmonic terms, dash-dotted lines by adding the quartic terms, and the solid line by adding both cubic and quartic terms to the one-particle potential function.

The section of equipotential surfaces in the *yz* plane (perpendicular to the atomic mirror plane) shown in Fig. 2(*b*) illustrates the symmetric distortion of the effective one-particle potential function due to the quartic terms (contribution of the third order term is now identically zero). Fig. 2(*c*) shows the combined influence of the symmetric and antisymetric distortions in a mirror plane.

The study of thermal vibrations in Zn is being pursued by neutron single crystal studies at a number of elevated temperatures.

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Molecular Images of Thin-Film Polymorphs and Phase Transformations in Metal-Free Phthalocyanine

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Abstract

Molecular imaging of metal-free phthalocyanine, prepared expitaxically on KCl, showed two polymorphs. The unit-cell constants, measured from the *ac* projection, differed from previously quoted values and this was attributed to the effect of the preparation substrate. The transformation of one phase into another was apparently martensitic with lamellae of the opposite phase being present in both polymorphs.

Polymorphism is a common phenomenon in molecular crystals and the existence of polymorphs of phthalo-

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