Acta Cryst. (1977). A33, 351–354

Anharmonicity of Lattice Vibrations in Zinc by Elastic Neutron Scattering

BY M. MERISALO

Department of Physics, University of Helsinki, SF-00170 Helsinki 17, Finland

AND F. K. LARSEN

Department of Inorganic Chemistry, University of Aarhus, DK-8000 Aarhus C, Denmark

(*Received* 27 *September* 1976; *accepted* 10 *October* 1976)

The form of the effective anharmonic one-particle potential up to quartic terms is given and the expression of the temperature factor is derived for atoms occupying the sites of the point-group symmetry $\bar{6}m2$. The theory is applied to the analysis of the elastic thermal-neutron scattering data from a single crystal of Zn measured at 295 K and corrected for extinction and inelastic scattering contamination. The data show significant quartic terms. The values obtained for the anharmonic potential parameters correspond to the mean-square amplitudes $\langle u_x^2\rangle = 0{\cdot}0114$ (3) Å^2 and $\langle u_z^2\rangle = 0{\cdot}0257$ (5) Å^2 of the atomic vibrations in the principal directions. The present results are compared with other recent determinations. The discrepancy of the experimental values with theoretical calculations can be accounted for in full by constant-volume anharmonic effects.

1. Introduction

Rigorous lattice-dynamical calculation of anharmonic contributions to the measured intensities of the elastic-scattering pattern of X-rays and neutrons is extremely complex, and has been carried out thoroughly for only a few very simple crystal structures (see, for example, Maradudin & Flinn, 1963). An alternative approach is the treatment of the crystal as an Einstein solid (a system of independent anharmonic oscillators), whereby the real crystal potential is replaced by an effective one-particle potential. In spite of its simplicity, the model reproduces the main results of the rigorous lattice-dynamical treatment. A comprehensive review of the theory and the expression for the temperature factor of an atom in a cubic crystalline field have been presented by Willis (1969). A number of recent X-ray and neutron diffraction experiments on various cubic compounds have demonstrated conclusively the need to consider anharmonic effects in interpreting elastic-scattering data (for references, see Cooper & Rouse, 1973; Willis & Pryor, 1975; Prager & Harvey, 1975).

In the present study the extension of the isolated-atom formalism is made to the hexagonal close-packed structure which has been the object of growing interest in the past decade. The expression for the anharmonic temperature factor is derived and applied to analysis of the elastic neutron-scattering data of zinc in which significant anharmonicity is indicated by the existence of the finite third-order elastic constants (Schwartz & Elbaum, 1970) and by elastic X-ray-scattering results (Skelton & Katz, 1968).

2. Theory

In the approximation of an anharmonic Einstein solid, the vibration of each atom in the crystal is assumed to be governed by an effective one-particle potential, $V(\mathbf{u})$, representing the potential experienced by the atom under small displacements, $\mathbf{u}$, when all the neighbouring atoms are kept fixed. The form of the anharmonic potential $V(\mathbf{u})$ is determined by the site symmetry of the atom concerned. A convenient expression is obtained by expanding the potential 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. Having regard to the site symmetry of the atoms ($\bar{6}m2$; u_2 parallel to the 2-axis or perpendicular to m, and u_3 parallel to $\bar{6}$) in the hexagonal close-packed structure, $V(\mathbf{u})$ will take the form

$$V(\mathbf{u}) = V_0 + u^2(\alpha_{20}K_{20} + \beta_{00}) + u^3\alpha_{33}K_{33} + u^4(\alpha_{40}K_{40} + \beta_{20}K_{20} + \gamma_{00}), \quad (1)$$

where terms up to fourth order have been retained. Here V_0, α_{ij}, β_{ij}, and γ_{ij} are constants of the potential, $u^2 = u_1^2 + u_2^2 + u_3^2$, and K_{ij} are the symmetry-adapted harmonics given by

$$\begin{aligned} u^2K_{20} &= \tfrac{1}{2}(3u_3^2 - u^2) \\ u^3K_{33} &= u_1^3 - 3u_1u_2^2 \\ u^4K_{40} &= \tfrac{1}{8}(35u_3^4 - 30u_3^2u^2 + 3u^4) \end{aligned} \quad (2)$$

with the normalization $\max\{K_{ij}\} = 1$.

The quadratic term in the potential (1) is appropriate to a harmonic crystal with vibrational anisotropy, while the cubic and quartic terms represent anharmonic modifications to $V(\mathbf{u})$.

The temperature factor $T(\mathbf{Q})$ for an atom in an Einstein solid can be evaluated in the classical or high-temperature limit from (Willis, 1969)

$$T(\mathbf{Q}) = \frac{\int_{-\infty}^{\infty}\int\int\int \exp[-V(\mathbf{u})/k_BT]\exp(i\mathbf{Q}\cdot\mathbf{u})\mathrm{d}u_1\mathrm{d}u_2\mathrm{d}u_3}{\int_{-\infty}^{\infty}\int\int\int \exp[-V(\mathbf{u})/k_BT]\mathrm{d}u_1\mathrm{d}u_2\mathrm{d}u_3} \quad (3)$$

representing the ensemble average of $\exp(i\mathbf{Q}.\mathbf{u})$, $\mathbf{Q}$ being the scattering vector. By assuming that the anharmonic terms in (1) are small compared with k_BT, one can approximate $\exp[-V(\mathbf{u})/k_BT]$ in (3) by the expansion

$$\exp[-V(\mathbf{u})/k_BT]=\exp(-V_0/k_BT)\times\exp(-\tfrac{1}{2}A^2u_1^2-\tfrac{1}{2}A^2u_2^2-\tfrac{1}{2}B^2u_3^2)\left\{1-\frac{\alpha_{33}}{k_BT}u^3K_{33}-\frac{1}{k_BT}u^4(\alpha_{40}K_{40}+\beta_{20}K_{20}+\gamma_{00})\right\}, \quad (4)$$

where the notations $A^2=(2\beta_{00}-\alpha_{20})/k_BT$ and $B^2=2(\beta_{00}+\alpha_{20})/k_BT$ have been adopted. The integrals obtained by substitution of the expansion (4) into the expression (3) for the temperature factor can be conveniently evaluated by applying the result:

$$\int_{-\infty}^{\infty}H_n(ax)\exp(-\tfrac{1}{2}a^2x^2)\exp(2\pi ihx)\mathrm{d}x=i^n\frac{\sqrt{(2\pi)}}{a}H_n\left(\frac{2\pi h}{a}\right)\exp\left(-\frac{2\pi^2h^2}{a^2}\right) \quad (5)$$

for the Fourier transform of Hermite orthogonal functions $H_n(x)\exp(-\frac{1}{2}a^2x^2)$. Thus the temperature factor for an atom in a potential field defined by (1) and (2) can be expressed as

$$\begin{aligned}T(\mathbf{Q})=N^{-1}&\exp[-\tfrac{1}{2}(s_1^2+s_2^2+s_3^2)]\\&\times\left\{1+i\frac{\alpha_{33}}{k_BTA^3}(s_1^3-3s_1s_2^2)\right.\\&-\frac{(3\alpha_{40}-4\beta_{20}+8\gamma_{00})}{8k_BTA^4}\\&\times(s_1^4+s_2^4-8s_1^2-8s_2^2+2s_1^2s_2^2+8)\\&-\frac{(\alpha_{40}+\beta_{20}+\gamma_{00})}{k_BTB^4}(s_3^4-6s_3^2+3)\\&\left.-\frac{(6\alpha_{40}-\beta_{20}-4\gamma_{00})}{2k_BTA^2B^2}(1-s_3^2)(s_1^2+s_2^2-2)\right\}, \quad (6)\end{aligned}$$

where

$$\begin{aligned}N=1&-\frac{3\alpha_{40}}{k_BT}(A^{-4}+B^{-4}-2A^{-2}B^{-2})\\&-\frac{\beta_{20}}{k_BT}(-4A^{-4}+3B^{-4}+A^{-2}B^{-2})\\&-\frac{\gamma_{00}}{k_BT}(8A^{-4}+3B^{-4}+4A^{-2}B^{-2}). \quad (7)\end{aligned}$$

The quantities s_1, s_2, s_3 are related to the Miller indices h, k, l of the reflexion by

$$s_1=\frac{2\pi(2h+k)}{Aa_1\sqrt{3}},\quad s_2=\frac{2\pi k}{Aa_2},\quad s_3=\frac{2\pi l}{Ba_3} \quad (8)$$

where a_1, $a_2(=a_1)$, and a_3 are the conventional cell dimensions of the hexagonal unit cell.

The factor $\exp[-\frac{1}{2}(s_1^2+s_2^2+s_3^2)]$ in (6) represents the harmonic anisotropic temperature factor, and it is readily found that the conventional temperature-factor coefficients β_{ij} are related to the constants α_{20} and β_{00} of the potential by

$$\beta_{11}=\beta_{22}=\frac{4\pi^2k_BT}{3a_1^2(\beta_{00}-\frac{1}{2}\alpha_{20})},\quad \beta_{33}=\frac{\pi^2k_BT}{a_3^2(\beta_{00}+\alpha_{20})}. \quad (9)$$

Anharmonic perturbation introduced in (1) manifests itself in expression (6) for the temperature factor through the terms in curly brackets which modify the harmonic contribution in reciprocal space.

3. Measurements

Integrated intensities of Bragg reflexions from the zinc single crystal were measured at room temperature using a Hilger–Ferranti four-circle diffractometer at the Danish Atomic Energy Commission Research Establishment, Risø. The 002 reflexion from a Be monochromator crystal provided an incident neutron beam of wavelength 1·070 Å. Measurements were made with the ω–2θ step-scanning technique with step length 0·08° in 2θ. The FWHM of the reflexions was found to be 0·5 and 1·2° near the focusing position (at 35° in 2θ) and at $2\theta=80°$, respectively. The total scan width w was determined by $w=2{\cdot}5°\tan\theta+6{\cdot}28°$. The single crystal used was a rectangle of dimensions 2·4 × 3·2 × 4·4 mm shaped by arc-cutting from a crystal grown at the Helsinki University of Technology.

The measured integrated intensities were corrected for the long-term systematic decrease observed in the standard reflexions (less than 2% over the data collection period of about four weeks). Correction for absorption was made by the Gaussian integration method (Coppens, Leiserowitz & Rabinovich, 1965) with the neutron absorption coefficient $\mu=0{\cdot}039\ \mathrm{cm}^{-1}$. Thermal inelastic-scattering contamination was subtracted from the measured intensities by applying the anisotropic one-phonon approximation giving proper consideration to the measuring geometry (for details see Merisalo & Kurittu, 1976).

550 reflexions with $\sin\theta/\lambda\leq 0{\cdot}78\ \text{Å}^{-1}$ were measured, of which 34 were unrelated by symmetry. The internal agreement of the symmetry-related reflexions was good, except for 100 and 110 which were then omitted from the final refinement.

4. Data analysis

(a) *Harmonic model*

The analysis was initiated by fitting the data by the method of least squares to a harmonic model. Zinc

conforms to the space group $P6_3/mmc$ with one atom per asymmetric unit in the special position 2(*c*). This gives the constraints $\beta_{11}=\beta_{22}=2\beta_{12}\neq\beta_{33}$, $\beta_{13}=\beta_{23}=0$ for the thermal parameters. Thus, the least-squares refinement involved four variables: the scale factor, the isotropic extinction parameter (Coppens & Hamilton, 1970) and the two thermal parameters β_{11} and β_{33}. The value $0{\cdot}57\times10^{-12}$ cm (Bacon, 1972) for the scattering length was adopted, and the values $a_1=a_2=2{\cdot}664$ Å and $a_3=4{\cdot}945$ Å were assigned to the cell dimensions.

The refinement converged to a value of 1·45% for the crystallographic R value, defined as $R=\Sigma||F_o|-|F_{c,h}||/\Sigma|F_o|$, where F_o and $F_{c,h}$ are the observed and calculated structure factors respectively. Extinction corrections were found to be reasonably small for the size of the crystal, which adds to the credibility of the extinction model. Attempts to use an anisotropic model for extinction failed to give any better refinement, but indicated that the mosaicity was quite isotropic.

The values of F_o and $F_{c,h}$, along with standard deviations σ, extinction coefficients y, and relative contributions α from thermal inelastic scattering (y and α apply to F_o^2), are listed in Table 1, columns 2–6. The corresponding values of the mean-square amplitudes $\langle u_x^2\rangle=\langle u_y^2\rangle$ and $\langle u_z^2\rangle$ in directions parallel and perpendicular to the hexagonal axis were 0·0107 (2) and 0·0273 (3) Å^2 respectively.

(*b*) *Anharmonic model*

The observed structure factors, scaled and corrected for extinction by the least-squares fitting to the harmonic model [as discussed in § 4(*a*)], were taken as the data for the analysis of anharmonic effects. Thus it was assumed that the scale and extinction parameters are not correlated with either harmonic or anharmonic thermal parameters. This assumption was found to be valid, within experimental errors, by initial refinements.

The potential parameters were determined by minimizing the function MF given by

$$\mathrm{MF}=\sum||F_o|-|F_{c,ah}||^2W,$$

where $W=1/\sigma^2$, $F_{c,ah}=F(0)T(\mathbf{Q})$, $F(0)$ referring to the calculated structure factor with the atoms at rest, and $T(\mathbf{Q})$ is defined by equations (6)–(8). Minimization of MF was effected by a computer program which was developed so as to avoid the need for analytic evaluation of partial derivatives.

Because of strong correlation between the harmonic and anharmonic parameters, it was not possible to refine them simultaneously. In the final analyses, therefore, the harmonic parameters α_{20} and β_{00} were fixed and two models were considered. For model 1 the harmonic parameters are those obtained in § 4(*a*), whereas model 2 includes the values determined from the theoretical calculation of Barron & Munn (1967). The values of the anharmonic parameters are there-

Table 1. *Neutron diffraction data for zinc*

h	k	l	F_o	σ	α	y	$F_{c,h}$	$F_{c,ah}^{\text{model 1}}$	$F_{c,ah}^{\text{model 2}}$
0	0	2	1·059	0·005	0·005	0·762	1·044	1·047	1·048
0	0	4	0·800	0·004	0·028	0·901	0·801	0·805	0·807
0	0	6	0·501	0·003	0·077	0·962	0·515	0·502	0·503
1	0	1	0·945	0·005	0·004	0·788	0·928	0·927	0·927
1	0	2	0·505	0·003	0·009	0·934	0·502	0·503	0·503
1	0	3	0·781	0·004	0·018	0·883	0·778	0·782	0·783
1	0	4	0·381	0·002	0·034	0·970	0·385	0·387	0·388
1	0	5	0·539	0·003	0·055	0·951	0·547	0·546	0·547
1	0	6	0·246	0·001	0·082	0·989	0·248	0·243	0·243
1	0	7	0·314	0·002	0·115	0·983	0·322	0·303	0·302
1	1	2	0·936	0·005	0·018	0·859	0·926	0·926	0·926
1	1	4	0·716	0·004	0·044	0·921	0·711	0·717	0·717
1	1	6	0·451	0·002	0·095	0·967	0·457	0·454	0·452
2	0	0	0·475	0·002	0·015	0·947	0·486	0·482	0·481
2	0	1	0·813	0·004	0·017	0·880	0·823	0·818	0·817
2	0	2	0·459	0·002	0·023	0·964	0·445	0·444	0·444
2	0	3	0·697	0·003	0·033	0·925	0·690	0·694	0·694
2	0	4	0·345	0·002	0·048	0·981	0·342	0·345	0·345
2	0	5	0·484	0·002	0·070	0·963	0·485	0·490	0·489
2	0	6	0·224	0·001	0·095	0·992	0·220	0·219	0·218
2	1	0	0·419	0·002	0·029	0·968	0·431	0·424	0·424
2	1	1	0·721	0·004	0·031	0·918	0·731	0·720	0·720
2	1	2	0·400	0·002	0·037	0·976	0·395	0·392	0·392
2	1	3	0·622	0·003	0·047	0·944	0·613	0·615	0·614
2	1	4	0·304	0·002	0·075	0·985	0·303	0·307	0·307
2	1	5	0·434	0·002	0·101	0·968	0·430	0·439	0·437
2	2	0	0·684	0·003	0·053	0·918	0·707	0·685	0·686
2	2	2	0·647	0·003	0·072	0·935	0·647	0·637	0·638
3	0	0	0·750	0·004	0·039	0·908	0·796	0·779	0·779
3	0	2	0·730	0·004	0·046	0·918	0·729	0·722	0·722
3	0	4	0·563	0·003	0·083	0·947	0·560	0·568	0·568
3	1	0	0·342	0·002	0·066	0·980	0·340	0·328	0·329

fore appropriate only to the corresponding values of the harmonic parameters.

Initial analyses also showed that the value of the cubic anharmonic parameter α_{33} did not differ significantly from zero and it was subsequently fixed at $\alpha_{33}=0$.

The calculated structure factors are given in Table 1 and the final parameter values in Table 2. For both models the refinement converged at an R value of 1·18%.

5. Discussion

The value of the R factor ratio for the harmonic and anharmonic models is 1·23. A significance test [based on the significance tables of Hamilton (1965)] shows that the improvement resulting from inclusion of the quartic anharmonic parameters is indeed significant for both models at a level much less than 0·005.

Correlation between the harmonic and anharmonic parameters is clearly seen by comparing the results given in Tables 1 and 2. The R values as well as the calculated structure factors, are practically identical for both models. The values of the anharmonic parameters, on the other hand, show remarkable discrepancies. It is therefore concluded that a part of the anharmonic contribution is included in the harmonic parameters of model 1 and thus model 2 constitutes a more appropriate model for a discussion of the intrinsic anharmonic effects.

Table 2. *Final values of potential parameters for* Zn

	Model 1	Model 2	
α_{20}	−0·766 (10)	−1·109 (10)	$\times 10^{-12}$ erg Å^{-2}
β_{00}	1·511 (10)	1·841 (10)	$\times 10^{-12}$ erg Å^{-2}
α_{33}	0	0	$\times 10^{-12}$ erg Å^{-3}
α_{40}	2·77 (15)	1·33 (15)	$\times 10^{-12}$ erg Å^{-4}
β_{20}	−1·32 (15)	6·52 (20)	$\times 10^{-12}$ erg Å^{-4}
γ_{00}	−0·04 (10)	−6·13 (20)	$\times 10^{-12}$ erg Å^{-4}

These effects can be discussed conveniently by studying some integral parameters characterizing the thermal smearing function as a whole rather than the harmonic and anharmonic parameters themselves separately, for example, the mean-square amplitudes of the atomic vibrations in the principal directions. In the high-temperature limit these can be evaluated as an ensemble average by the Boltzmann distribution function such that

$$\langle u_p^2\rangle = \frac{\int u_p^2 \exp\left[-V(u)/k_BT\right]}{\int \exp\left[-V(u)/k_BT\right]}, \quad p=x,z.$$

For model 2 this leads to the values $\langle u_x^2\rangle=0{\cdot}0114\,(3)$ Å^2 and $\langle u_z^2\rangle=0{\cdot}0257$ (5) Å^2. The deviations of these results from the calculated values $\langle u_x^2\rangle=0{\cdot}0085$ (5) Å^2 and $\langle u_z^2\rangle=0{\cdot}0276$ (15) Å^2 (Barron & Munn, 1967) appropriate to the model represent the effects of intrinsic anharmonicity. Thus the present results indicate a considerable and significant increase (about 35%) of the mean-square amplitude and a softening of the potential function in the basal plane, whereas the decrease of the mean-square amplitude along the hexagonal axis remains uncertain, within the experimental error. The present results are also in excellent agreement with the values $\langle u_x^2\rangle=0{\cdot}0112$ (3) Å^2 and $\langle u_z^2\rangle=0{\cdot}0259$ (10) Å^2 determined from single-crystal X-ray diffraction intensities by Skelton & Katz (1968) and support their suggestion that the discrepancy with the calculated values of Barron & Munn (1967) may be caused by constant-volume anharmonic effects.

Table 3. *Values of mean-square amplitudes* (Å^2) *along the principal axes of zinc*

Reference	$\langle u_x^2\rangle$	$\langle u_z^2\rangle$
Barron & Munn (1967)	0·0085 (5)	0·0276 (15)
Skelton & Katz (1968)	0·0112 (3)	0·0259 (10)
Present harmonic model	0·0107 (3)	0·0273 (5)
Present anharmonic model 1	0·0113 (3)	0·0260 (5)
Present anharmonic model 2	0·0114 (3)	0·0257 (5)

For model 1 the values $\langle u_x^2\rangle=0{\cdot}0113$ (2) Å^2 and $\langle u_z^2\rangle=0{\cdot}0260$ Å^2 were obtained. These are consistent with those of model 2 and emphasize the fact that although anharmonic parameters can be evaluated from the present data only by fixing the harmonic parameters at appropriate values, the mean-square amplitudes are rather independent of the particular choice of parameters. The values of the mean-square amplitudes are summarized in Table 3.

We are indebted to Professor K. Kurki-Suonio for valuable discussions, and to Miss S. Rosten for her invaluable help with the computational work. This study was financially supported by the National Council for Science, Finland and by the University of Helsinki (MM).

References

BACON, G. E. (1972). *Acta Cryst.* A**28**, 357–358.
BARRON, T. H. K. & MUNN, R. W. (1967). *Acta Cryst.* **22**, 170–173.
COOPER, M. J. & ROUSE, K. D. (1973). *Acta Cryst.* A**29**, 514–520.
COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* A**26**, 71–83.
COPPENS, P., LEISEROWITZ, L. & RABINOVICH, D. (1965). *Acta Cryst.* **18**, 1035–1038.
HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510.
MARADUDIN, A. A. & FLINN, P. A. (1963). *Phys. Rev.* **129**, 2529–2547.
MERISALO, M. & KURITTU, J. (1976). *Report Series in Physics*, No. 120, Univ. of Helsinki.
PRAGER, P. R. & HARVEY, G. G. (1975). *Acta Cryst.* A**32**, 780–783.
SCHWARTZ, K. D. & ELBAUM, C. (1970). *Phys. Rev.*(*B*), **1**, 1512–1517.
SKELTON, E. F. & KATZ, J. L. (1968). *Phys. Rev.* **171**, 801–808.
WILLIS, B. T. M. (1969). *Acta Cryst.* A**25**, 277–300.
WILLIS, B. T. M. & PRYOR, A. W. (1975). *Thermal Vibrations in Crystallography*. Cambridge Univ. Press.