to believe that Bragg intensities fitted with a split-atom model necessarily correspond to a static distribution of atoms about fractionally occupied sites. In the present model, for example, the atoms are continuously hopping across the potential barrier for $T > T_C$ and even below $T_C$ some hopping occurs until the temperature is low enough for the ordering to be complete. Nevertheless, a split-atom model would give a reasonable fit to the corresponding Bragg scattering [see Mair (1983*b*), where a split-atom model is used to fit probability densities for a one-dimensional analogue of the present data].

A CSIRO Cyber 205 grant is gratefully acknowledged.

**References**

COWLEY, J. M. (1975). *Diffraction Physics*, p. 149. Amsterdam: North-Holland.
ITOH, K. (1984). *J. Phys. Soc. Jpn*, **53**, 2049-2053.
JOHNSON, C. H. J. & MAIR, S. L. (1985). *J. Phys. C*, **18**, 67-75.
KADANOFF, L. P. (1966). *Nuovo Cimento B*, **44**, 276-305.
LANDER, G. H. & BROWN, P. J. (1985). *J. Phys. C*, **18**, 2017-2024.
MAIR, S. L. (1983*a*). *J. Phys. C.* **16**, 4811-4825.
MAIR, S. L. (1983*b*). *J. Phys. C*, **16**, 5591-5604.
MAIR, S. L. (1984*a*). *Phys. Rev. B*, **30**, 6560-6564.
MAIR, S. L. (1984*b*). *Solid State Commun.* **52**, 335-337.
MAIR, S. L. (1986). *J. Phys. C*, **19**, 6321-6338.
MAIR, S. L. (1987). *Aust. J. Phys.* Submitted.
NELMES, R. J., KUHS, W. F., HOWARD, C. J., TIBBALLS, J. E. & RYAN, T. W. (1985). *J. Phys. C*, **18**, L1023-L1030.
SAKATA, M., HARADA, J., COOPER, M. J. & ROUSE, K. D. (1980). *Acta Cryst.* A**36**, 7-15.
SCHNEIDER, T. & STOLL, E. (1980). *Phys. Rev. B*, **22**, 5317-5338.
WILLIS, B. T. M. & PRYOR, A. W. (1975). *Thermal Vibrations in Crystallography*, p. 210. Cambridge Univ. Press.

*Acta Cryst.* (1987). A**43**, 694-698

# Anharmonicity of Atomic Vibrations in Magnesium by Measurement of Almost-Forbidden Reflections

BY M. JÄRVINEN AND J. SOININEN

*Lappeenranta University of Technology, Box* 20, *SF*-53851 *Lappeenranta, Finland*

AND M. MERISALO

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

(*Received* 17 *March* 1986; *accepted* 15 *April* 1987)

## Abstract

The X-ray intensities of almost-forbidden reflections 301 and 303 in a single crystal of magnesium have been measured at 293 K. Effective monochromatization by appropriate electronics was utilized to increase the observability of these weak reflections. The data are interpreted in terms of atomic vibrations by application of a quantum-statistical one-particle formalism that allows anharmonic contributions to the atomic temperature factor. A value of $-0{\cdot}43\,(3)$ eV Å$^{-3}$ is obtained for the third-order anharmonic parameter, the negative sign being deduced from the coordination. This outcome is in accordance with earlier results concerning anharmonic vibrations.

## 1. Introduction

A proper consideration of symmetry requirements has an important implication in diffraction studies. For some simple crystal structures, in which all atoms are at special positions and not located at the centre of symmetry, the conventional special extinction rules may be violated. Consequently, weak 'forbidden' reflections - more properly termed almost-forbidden reflections - may occur. X-ray and neutron diffraction studies on the first and best known case - the 222 reflection in diamond structures - have demonstrated both non-sphericity of valence-charge density and anharmonicity of thermal vibrations (Roberto & Batterman, 1970; Keating & Nunes, 1971; Bilderback & Colella, 1975). Recently, almost-forbidden reflections have been observed in hexagonal close-packed zinc (Merisalo, Järvinen & Kurittu, 1978) and cadmium (Merisalo, Peljo & Soininen, 1978), and in tetragonal tin (Merisalo & Järvinen, 1978). In all these studies the data were interpreted in terms of anharmonicity of lattice vibrations. The most recent measurement on the almost-forbidden reflection 202 of white tin (Merisalo & Soininen, 1979) revealed the

0108-7673/87/050694-05$01.50 © 1987 International Union of Crystallography

antisymmetric bond-charge component in the valence-charge density.

In this paper we report the results of an X-ray diffraction study of the almost-forbidden reflection in magnesium. The study was carried out to gain more detailed information about anharmonic contributions to the atomic vibrations in magnesium. A general objective is to extend studies on HCP elements in order to find possible systematics and correlations between the anharmonic parameter and various physical properties of these crystals.

## 2. Model for atomic vibration

The diffraction technique is, by definition, sensitive only to the one-particle properties of the atomic vibrations. Therefore, a proper phenomenological approach is to parametrize the thermal smearing function (TSF) and the atomic temperature factor (ATF) in terms of the one-particle-potential (OPP) model of atomic vibrations, in which the crystal is treated as a system of uncoupled anharmonic oscillators (Dawson, Hurley & Maslen, 1967; Willis, 1969; Willis & Pryor, 1975).

Both magnesium atoms of the h.c.p. unit cell sit at special positions of $\bar{6}m2$ site symmetry. With a choice of local Cartesian coordinate axes $u_1$, $u_2$, $u_3$ so that $u_1 \| 2$, $u_2 \perp m$, $u_3 \| \bar{6}$ (Fig. 1), and if terms up to third order are retained, the site-symmetrized expansion of the one-particle potential $V(u)$ in terms of the Cartesian components $u_1$, $u_2$, $u_3$ of the atomic displacement **u** can be written as (Kurki-Suonio, Merisalo & Peltonen, 1979; Kara & Merisalo, 1982)

$$V(u) = \beta_1(u_1^2+u_2^2)+\beta_2 u_3^2+\gamma(u_1^3-3u_1u_2^2), \quad (1)$$

where $\beta_1$ and $\beta_2$ are the harmonic force constants and $\gamma$ is the third-order anharmonic parameter.

In the present study the ratio of the sample temperature ($T = 292$ K) and the Debye temperature is about 0·7. Consequently, a quantum rather than a classical approach should be used in relating OPP to TSF and ATF (Dawson, 1975; Mair & Wilkins, 1976, 1981; Kara & Merisalo, 1982; Larsen, Brown, Lehmann & Merisalo, 1982). Quantum-statistical expressions in the OPP formalism for the h.c.p. structure have been given by Kara & Merisalo (1982). In their notation, the TSF is now written as

$$t(u;T) = (b_1^2b_2/\pi^3)^{1/2}\exp[-b_1(u_1^2+u_2^2)-b_2u_3^2] \times[1-\gamma A(\hbar\omega_1/k_BT)(u_1^3-3u_1u_2^2)], \quad (2)$$

where

$$A(\hbar\omega_1;T) = (1/\hbar\omega_1)\sinh^{-3}(\hbar\omega_1/k_BT) \times[13/3-(11/2)\cosh(\hbar\omega_1/k_BT) +\cosh(2\hbar\omega_1/k_BT) +(1/6)\cosh(3\hbar\omega_1/k_BT)], \quad (3)$$

and $b_i$ and $\omega_i$ are related to force constants $\beta_i$ ($i = 1, 2$) by

$$b_i = (m\omega_i/\hbar)\tanh(\hbar\omega_i/2k_BT) \quad (4)$$

$$\omega_i = (2\beta_i/m)^{1/2}. \quad (5)$$

In these expressions $\omega_i$ is the angular frequency of the oscillating atom of mass $m$, $k_B$ is the Boltzmann constant, and $T$ is the absolute temperature.

The mean-square amplitudes of atomic vibrations are obtained from the expression

$$u_i^2 = (\hbar/2m\omega_i)\coth(\hbar\omega_i/2k_BT), \quad i = x, z.$$

The quantum-statistical ATF - the Fourier transformation of the TSF - is given by

$$T(\mathbf{H}) = \exp(-H_1^2/4b_1-H_2^2/4b_1-H_3^2/4b_2) \times[1+i\gamma(1/2b_1)^3A(\hbar\omega_1;T)(H_1^3-3H_1H_2^2)] = T_s(\mathbf{H})+iT_a(\mathbf{H}), \quad (6)$$

where the Cartesian coordinates of the diffraction vector $\mathbf{H}(hkl)$ are now $H_1 = 2\pi(2h+k)/a\sqrt{3}$, $H_2 = 2\pi k/a$, $H_3 = 2\pi l/c$, $h$, $k$, $l$ are the Miller indices and $a$, $c$ the h.c.p. cell dimensions. $T_s(\mathbf{H})$ and $T_a(\mathbf{H})$ are the symmetric and antisymmetric parts of the ATF. The two atoms in the h.c.p. unit cell are related by a centre of inversion. Hence, $T_a(\mathbf{H})_{\text{atom1}} = -T_a(\mathbf{H})_{\text{atom2}}$ and the structure factor comes out as (Larsen *et al.*, 1982)

$$F(\mathbf{H}) = \pm 2f\{T_s(\mathbf{H})\cos[2\pi(h+2k)/3+l/4] -T_a(\mathbf{H})\sin[2\pi(h+2k)/3+l/4]\}, \quad (7)$$

where $f$ is the atomic scattering factor.

The second term in this expression is a correction term arising from anharmonicity. It is seen from (6) that $T_a(\mathbf{H})$ vanishes by symmetry only if $h = k$. According to the conventional extinction rule all reflections with $h = k+3n$ and $l$ odd ($n$ is any integer) are forbidden. This is now exact only for $n = 0$; all other reflections are regular though they can be expected to be very weak (*cf.* Kurki-Suonio, 1970). Thus these reflections can be termed 'almost-forbidden' reflections. In the range $(\sin\theta)/\lambda < 1{\cdot}6$ Å$^{-1}$ ten reflections of this sort can be found. In the measurements with Mo $K\alpha$ radiation only the reflections 301 and 303 are to be measured.

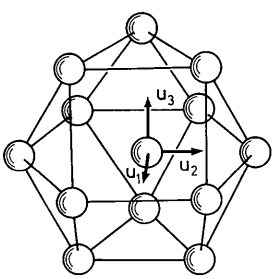


Fig. 1. The surroundings of the magnesium atom. $u_1$, $u_2$, $u_3$ are the local Cartesian coordinate axes.

### 3. Experimental

Earlier diffraction experiments on h.c.p. elements Zn (Merisalo, Järvinen & Kurittu, 1978) and Cd (Merisalo, Peljo & Soininen, 1978) show that the almost-forbidden reflections are really weak. For magnesium, for which the $c/a$ ratio is nearly ideal, the situation can be expected to be even more unfavourable. To increase observability of these feeble reflections a novel installation was constructed for the present experiment. Instead of the use of the crystal monochromatization an effective monochromatization was accomplished by using appropriate electronics. The scattered radiation was measured with a Ge detector that had an energy resolution better than 3% in the region of the Mo $K\alpha$ radiation. A single-channel analyser was used to discriminate the rest of the energy spectrum. Furthermore, an ordinary foil-filtering technique was used to reduce the part of the modified high-energy radiation passing through the energy window of the single-channel analyser.

The measurements were made using a highly stabilized X-ray generator operating at 35 kV and 30 mA and Mo radiation passing through a Zr filter. Test experiments carried out on a tin single crystal indicated that use of the previously mentioned techniques considerably reduced the collection time for an almost forbidden reflection compared with using a crystal monochromator (Merisalo, Peljo & Soininen, 1978). The magnesium single-crystal sample was supplied by Metals Research Co. It was grown by the Bridgeman method with the $[h0h]$ direction along the cylinder axis.

A 5 mm thick slab was cut with a spark saw. The flat surfaces were ground on water-cooled emery paper and then polished electrolytically in a solution of 1:4 perchloric acid and methyl alcohol using a controlled low-temperature technique (Räty, Lindroos, Saarinen, Forsten & Miekk-oja, 1966).

The crystal was mounted on a computer-controlled four-circle diffractometer and aligned carefully in the 301 and 303 reflection positions with the aid of the strong allowed reflections 602 and 202, 404 respectively. The values of the angles between the crystal surface and the reflecting-plane normal were 4 and 13° for the forbidden reflections 303 and 301, respectively.

For mapping the multiple-scattering events the crystal was rotated about the reflection-plane normal. The diffraction pattern is plotted in Fig. 2, which also shows an azimuthal angle range free from multiple-scattering events. The arrow indicates the point used for final measurements (Merisalo, Järvinen & Kurittu, 1978).

The primary beam was collimated with two circular pinholes of diameter 1 mm. All the reflected energy fell entirely into the detector aperture. A conical scattering shield, just wide enough for reflected radiation to pass, was placed in front of the detector aperture to minimize the parasitic scattering contamination. For each reflection a range of 6° was measured using an $\omega$-$2\theta$ step-scanning mode with step length 0·05° in $2\theta$. The counting time was 5 min/point and each reflection was measured five times in order to obtain statistical accuracy better than 10%. A typical rocking curve is shown in Fig. 3. The background was subtracted by fitting a second-order polynomial to the background (Merisalo, Järvinen & Kurittu, 1978). The observed integrated intensities were corrected for TDS contamination by use of the program *SXTDS*1 (Kurittu & Merisalo, 1977) based on the anisotropic one-phonon approximation (Merisalo & Kurittu, 1978). The elastic constants measured by Slutsky & Garland (1957) were used for TDS calculations giving corrections: $\alpha(301) = 0{\cdot}04$, $\alpha(303) = 0{\cdot}05$, $\alpha(505) = 0{\cdot}18$ and $\alpha(602) = 0{\cdot}22$. The absolute scale of the observed structure factors $F(301)$ and $F(303)$ was determined by measuring the integrated intensities relative to those of the allowed reflections 602 and 505, respectively.

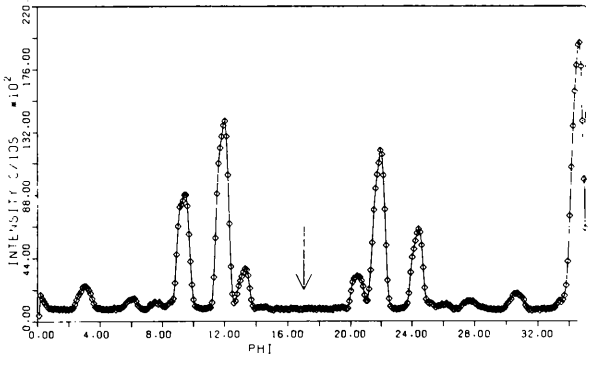


Fig. 2. An *Umweganregung* profile of the 303 reflection in magnesium.

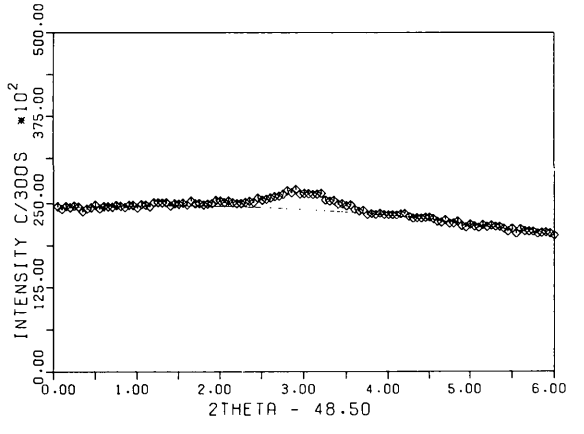


Fig. 3. Rocking curve for the 303 reflection in magnesium. Solid curve corresponds to the fitted background.

Table 1. *Experimental values of structure factors* $F(\mathbf{H})$ *of almost-forbidden reflections* 301 *and* 303 *in magnesium together with corresponding values of the antisymmetric part* $T_a(\mathbf{H})$ *of ATF and the anharmonic force constant* $\gamma_{qm}$ *(in units of* eV Å$^{-3}$*); values of anharmonic force constant* $\gamma_{cl}$ *based on a classical treatment (Merisalo, Järvinen & Kurittu,* 1978*) are given for comparison*

| *hkl* | $(\sin\theta)/\lambda$ (Å$^{-1}$) | F(H) | $T_a(\mathbf{H})$ | $\gamma_{qm}$ | $\gamma_{cl}$ |
|---|---|---|---|---|---|
| 301 | 0·55 | 0·107 (11) | 0·0135 | −0·45 (3) | −0·42 |
| 303 | 0·61 | 0·097 (10) | 0·0110 | −0·41 (3) | −0·36 |

The effects of extinction at the 301 and 303 reflections can be assumed to be small, owing to the extremely weak intensity involved. At the 505 and 602 reflections the effects of extinction were ascertained to be less than 4% by comparison of their intensities with the more intense reflection, 404.

The absorption corrections, which take into account the variation of inclination angles between the normals of different reflecting planes and the normal of the extended crystal face, were calculated after Mair, Prager & Barnea (1971).

The values of the anharmonic parameters were calculated from (3)–(7). In these calculations the Rothaan–Hartree–Fock values for the atomic scattering factors (*International Tables for X-ray Crystallography*, 1974) and the values of Cromer & Liberman (1970) for the dispersion corrections were used. The mean-square amplitudes were calculated from the experimental result $B_{\mathbf{H}} = 1{\cdot}25$ Å$^2$ of Laursen & Olsen (1979). Because the temperature factor $B_{\mathbf{H}}$ for magnesium is almost isotropic at room temperature, as shown by Sledziewska-Blocka & Lebech (1976), we used for the mean-square amplitudes the classical form

$$B_{\mathbf{H}} = 8\pi^2 u^2$$

with

$$u_x^2 = u_z^2 = 0{\cdot}0158 \text{ Å}^2.$$

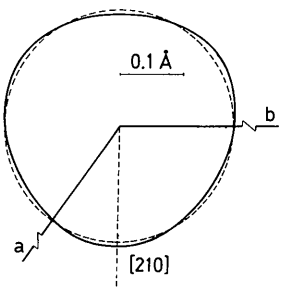


Fig. 4. The equipotential contours $V(u) = 0{\cdot}025$ eV of the potential in the basal plane of the magnesium crystal. Dotted curve corresponds to the harmonic model, solid curve to the anharmonic model.

The experimental values of the structure factor of the almost-forbidden reflections 301 and 303, the corresponding antisymmetric part of the atomic temperature factor, and the third-order anharmonic force constant are given in Table 1.

## 4. Discussion

The final values shown in Table 1 manifest excellent agreement between the two independent determinations of $\gamma_{qm}$.

It is to be noted that the measurement of the intensity of an almost-forbidden reflection yields the absolute value of $\gamma_{qm}$. However, from the coordination of the nearest neighbours in Fig. 1 it can be anticipated that the potential is softened towards the side which is part of the rectangular configuration of the neighbouring atoms and hardened against the side which is part of the triangular configuration of the neighbouring atoms [see also Larsen, Lehmann & Merisalo (1980)].

The thermal vibrations are more pronounced in the [210] direction (*i.e.* along the $u_1$ axis) than predicted by the harmonic model. This corresponds to the negative sign for $\gamma_{qm}$ as indicated in Table 1. This picture is identical to that arrived at in our earlier studies. [See also Juretschke & Barnea (1986).]

A qualitative visualization of the role of the third-order anharmonic term of the potential can be made in terms of equipotential contours (Fig. 4) or in terms of the probability density function (*i.e.* Edgeworth map) with a result corresponding to that shown by Larsen *et al.* (1980).

The axial anisotropy about the hexagonal axis ($\bar{6}$ axis) implied by a non-zero value of $\gamma_{qm}$ is in accordance with the study of Srinivasan & Ramji Rao (1971) which shows slightly different values for the third-order elastic constants $C_{111}$ and $C_{222}$.

Since this paper was submitted, we have been informed that a yet unpublished neutron-diffraction study on the temperature dependence of thermal vibrations in magnesium has been carried out by S. Kraemmer and F. Krebs Larsen, Aarhus University, Denmark. Full sets of diffraction data were collected at 11 temperatures between 125 and 775 K and the analysis shows $\gamma(298\text{ K}) = 0{\cdot}13\ (4)$ eV Å$^{-3}$.

One of us (MJ) would like to thank the Technical University of Lappeenranta for support of this work.

### References

BILDERBACK, D. H. & COLELLA, R. (1975). *Phys. Rev. B*, **11**, 793–797.

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

DAWSON, B. (1975). *Advances in Structure Research by Diffraction Methods*, Vol. 6, edited by W. HOPPE & R. MASON. Braunschweig: Vieweg.

DAWSON, B., HURLEY, A. C. & MASLEN, V. W. (1967). *Proc. R. Soc. London Ser. A*, **298**, 289-306.
*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
JURETSCHKE, H. J. & BARNEA, Z. (1986). *Phys. Scr.* **33**, 167-168.
KARA, M. & MERISALO, M. (1982). *Philos. Mag. B*, **45**, 25-30.
KEATING, D. & NUNES, A. (1971). *Phys. Rev. B*, **4**, 2472-2478.
KURITTU, J. & MERISALO, M. (1977). *Report Series in Physics*, No. 132. Univ. of Helsinki, Finland.
KURKI-SUONIO, K. (1970). *Acta Cryst.* A**26**, 458-459.
KURKI-SUONIO, K., MERISALO, M. & PELTONEN, H. (1979). *Phys. Scr.* **19**, 57-63.
LARSEN, F. K., BROWN, P. J., LEHMANN, M. S. & MERISALO, M. (1982). *Philos. Mag. B*, **45**, 31-50.
LARSEN, F. K., LEHMANN, M. S. & MERISALO, M. (1980). *Acta Cryst.* A**36**, 159-163.
LAURSEN, J. & OLSEN, J. S. (1979). *Acta Cryst.* A**35**, 482-484.
MAIR, S. L., PRAGER, P. R. & BARNEA, Z. (1971). *J. Appl. Cryst.* **4**, 169-171.
MAIR, S. L. & WILKINS, S. W. (1976). *J. Phys. C*, **9**, 1145-1148.
MAIR, S. L. & WILKINS, S. W. (1981). *Acta Cryst.* A**37**, 264-266.
MERISALO, M. & JÄRVINEN, M. (1978). *Philos. Mag.* **37**, 233-400.
MERISALO, M., JÄRVINEN, M. & KURITTU, J. (1978). *Phys. Scr.* **17**, 23-25.
MERISALO, M. & KURITTU, J. (1978). *J. Appl. Cryst.* **11**, 179-183.
MERISALO, M., PELJO, E. & SOININEN, J. (1978). *Phys. Lett. A*, **67**, 80-82.
MERISALO, M. & SOININEN, J. (1979). *Phys. Rev. B*, **19**, 6289-6294.
RÄTY, R., LINDROOS, V., SAARINEN, A., FORSTEN, J. & MIEKKOJA, H. M. (1966). *J. Sci. Instrum.* **43**, 367-370.
ROBERTO, J. & BATTERMAN, B. W. (1970). *Phys. Rev. B*, **2**, 3220-3226.
SLEDZIEWSKA-BLOCKA, D. & LEBECH, B. (1976). *Acta Cryst.* A**32**, 150-153.
SLUTSKY, L. J. & GARLAND, C. W. (1957). *Phys. Rev.* **107**, 972-976.
SRINIVASAN, R. & RAMJI RAO, R. (1971). *J. Phys. Chem. Solids*, **32**, 1769-1788.
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.

*Acta Cryst.* (1987). A**43**, 698-702

# The Relative Mean-Square Displacement Amplitudes of Bonded Atoms; Evidence from X-ray Crystallography, Normal-Mode Analysis and Molecular Dynamics

BY I. HANEEF AND D. S. MOSS

*Laboratory of Molecular Biology, Department of Crystallography, Birkbeck College, Malet Street, London WC1E 7HX, England*

(*Received* 6 *November* 1986; *accepted* 15 *April* 1987)

## Abstract

The relatively rigid nature of covalent bonds imposes limits on the difference between the mean-square displacements of the bonded atoms projected in the bond direction $\Delta$(m.s.d.a.). Evidence from X-ray crystallography shows that for many small-molecule structures this difference is usually less than the mean-square vibration amplitude of the bond. In less well ordered structures, where libration is more significant, molecular-dynamics calculations suggest that $\Delta$(m.s.d.a.) values may be much larger. A model of the kinematics of a librating bond is proposed and it is shown that a first-order approximation to $\Delta$(m.s.d.a.) is dependent on both second and fourth curvilinear moments.

## Introduction

The relatively rigid nature of covalent bonds has been exploited in several ways in refining crystal structures and in investigating the mean-square atomic displacements derived therefrom.

Hirshfeld (1976) refined charge-deformation models of four small organic structures. He examined the mean-square displacement amplitudes (m.s.d.a.) of pairs of bonded atoms in the direction of the bond and showed that the difference $\Delta$(m.s.d.a.) was smaller in the charge-deformation model than in that which assumed spherical atoms. By assuming that covalently bonded pairs of atoms should have effectively equal m.s.d.a.'s along their mutual bond, he was able to assert the superiority of the charge-deformation model. For atoms at least as heavy as carbon Hirshfeld estimated that the mean-square amplitude differences along bonds should normally be well under 0·001 Å$^2$.

Rollett (1970) stated that when two atoms are joined by a covalent bond, the difference between the atomic-vibration amplitudes in the bond direction could not exceed the amplitude of the bond-stretching vibration which for a carbon–carbon bond he estimated at 0·06 Å. He proposed that this vibration amplitude might be used to impose a restraint on the thermal parameters of bonded atoms in least-squares refinement. Terms representing the difference

0108-7673/87/050698-05$01.50 © 1987 International Union of Crystallography