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Anharmonic Contributions to the Debye–Waller Factor for Zinc

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Anharmonic contributions to the Debye–Waller factor of Zn for vibrations parallel to the *c* axis were obtained from the temperature dependence of integrated intensities for Bragg scattering at high temperatures. The Mössbauer technique was used to measure the purely elastic scattering. Both Gaussian and non-Gaussian contributions were found to be important. Their magnitude and sign were derived from the experimental data.

1. Introduction

The suggestion that accurate measurements of the Debye–Waller (DW) factor can play an important role in the investigation of anharmonic effects in crystal dynamics has been investigated since the early days of X-ray diffraction (see, for example, Waller, 1927). A number of papers were then devoted to analysing the different anharmonic contributions to the DW factor (Krivoglaz & Tekhonova, 1961; Maradudin & Flinn, 1963; Kashiwase, 1965; Willis, 1969; Wolfe & Goodman, 1969). Accurate experiments, however, are difficult to perform either with X-rays or neutrons, because in order to display anharmonic effects, it is necessary to work at high temperatures and with high-order reflexions, and under these conditions the measured reflexions include quite a large amount of thermal diffuse scattering (TDS). A solution has been offered by the Mössbauer effect which allows the separation of the elastic intensity at Bragg peaks with an energy resolution of about 10^{-8} eV (O'Connor & Butt, 1963; Ghezzi, Merlini & Pace, 1969). Diffraction experiments using Mössbauer radiations made it possible to detect strong anharmonic contributions to the DW factor in NaCl (Butt & Solt, 1971) and in Al (Albanese & Ghezzi, 1973); moreover, the analysis of these contributions showed that non-Gaussian or 'anomalous' terms were important.

The present paper deals with the application of the Mössbauer technique to the measurement of both Gaussian and non-Gaussian terms of the DW factor in Zn crystals. Zn was chosen because of its low Debye temperature and melting point. The investigation was limited to the vibrations having non-zero components parallel to the *c* axis owing to the larger component of the mean-square displacement of the atoms in this direction when it is compared with the mean-square vibrational amplitude in the basal planes (Wollan & Harvey, 1937; Ryba, 1960; DeWames, Wolfram & Lehman, 1965; Barron & Munn, 1967; Skelton & Katz, 1968).

2. Experimental method

The separation of the γ-rays which are elastically scattered by the crystal from those which undergo inelastic scattering was made by using the same procedure described in a previous paper (Albanese, Ghezzi, Merlini & Pace, 1972). A 100 mCi ^{57}Co source diffused in a chromium matrix ($10\times 2{\cdot}5$ mm) was used together with a 310-stainless steel absorber 98% enriched in ^{57}Fe, with a thickness equal to 1 mg cm^{-2} of ^{57}Fe.

The 14·4 KeV photons were detected by a NaI(Tl) scintillation counter with a single-channel analyser adjusted to reject Zn $K\alpha$ fluorescence radiation. In addition, the amount of fluorescence radiation reaching the counter was reduced by inserting a 3 mm thick plexiglass filter in the scattered beam. The Zn crystals were 3 mm thick lamellae (15×15 mm) cleaved along the (0001) basal planes from a larger crystal with a purity better than 99·99%. They were kept within the furnace in an argon atmosphere in order to prevent oxidation during high-temperature measurements.

Using the geometry of the symmetric Bragg case, the integrated intensities of the 0002, 0004 and 0006 reflexions were measured in the temperature range 295–640 K. The temperature of the sample was kept constant within ±1 K. The crystal was rotated around the goniometer axis and the area under the elastic Bragg peaks was measured after having subtracted the inelastic scattering contributions (Compton scattering plus phonon scattering). Several temperature cyclings were performed in order to ascertain the temperature dependences of the integrated elastic intensities and particular care was taken to make sure that the diffraction peaks would maintain a regular shape. The fact that the experimental data were not significantly affected by modifications to the crystal perfection during the experiment can be proved by the regular behaviour of the intensity of the 0002 reflexion (see Fig. 1), which, being the lowest order reflexion, is in fact the one most sensitive to crystal perfection. With the wavelength used in this experiment ($\lambda=$

0·8602 Å), the calculated ratio between the two extreme values of the intensity for an ideally mosaic and a perfect absorbing crystal was 3·68 at $T=300$ K, which is considerably larger that the reproducibility of the experimental data.

3. Results and discussion

In order to ascertain the degree of perfection of the crystal, the integrated intensity for 0002, 0004 and 0006 reflexions was measured at room temperature by conventional X-ray apparatus using Mo $K\alpha$ radiation. Absolute values, obtained by measuring the intensity of the direct beam by means of calibrated stainless steel filters, are compared in Table 1 with the calculated ones for an ideally mosaic crystal and a perfect absorbing crystal. The harmonic approximation, with an X-ray Debye temperature $\Theta_z=166$ K (see below), was assumed in these calculations; the approximated analytical formula given by Hirsch & Ramachandran (1950) was used in the case of the perfect absorbing crystal. The experimental absolute values for the 0004 and 0006 reflexions are very near to the calculated ones for an ideally mosaic crystal. Moreover, the calculated temperature dependences of the integrated intensities for the two extreme cases of a mosaic and a perfect absorbing crystal are not very different. For example, for the 0004 reflexion, the two intensities at 600 K differ by 17% after they are arbitrarily assumed to be equal at 300 K. For these two reasons we shall assume in the following that in the present experiment the temperature dependences of the integrated intensity of the elastic Bragg peaks at the 0004 and 0006 reflexions are described with sufficient accuracy by taking them as proportional to the square of the Debye–Waller factor.

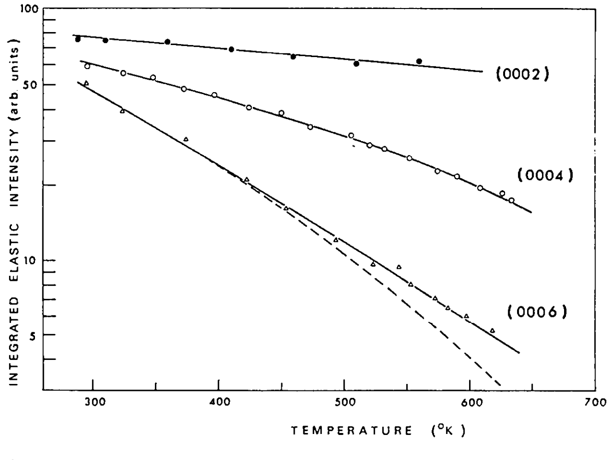

Fig. 1. Logarithm of the integrated elastic intensities *vs* temperature at the 0002, 0004 and 0006 Bragg peaks in Zn. The dashed line gives the temperature dependence for the 0006 reflexion as calculated from the 0004 data if non-Gaussian contributions to the DW factor were absent (see text).

Table 1. *Experimental absolute values* ($R_{\exp}$) *of integrated intensities as compared with the calculated ones for an ideally mosaic* (R_M) *and a perfect absorbing crystal* (R_P); *symmetric Bragg case*

hkil	R_M (10^{-5})	R_P (10^{-5})	$R_{\exp}$ (10^{-5})
0002	23·84	5·035	9·1 ± 0·05
0004	3·505	1·199	3·4 ± 0·15
0006	0·5265	0·2927	0·54 ± 0·03

Finally, the considerably high values of the integrated intensities with respect to the calculated ones for a perfect crystal suggest that the elastic intensity data were not appreciably affected by the possibility of multiple Bragg reflexions. This fact was also checked by observing that the intensity of 0004 and 0006 Bragg peaks did not change during rotation of the crystal azimuth.

Experimental values of the integrated elastic intensities of the 0002, 0004 and 0006 peaks are plotted in Fig. 1 *versus* temperature on a semilogarithmic scale.

Only 0004 and 0006 data were used to study anharmonic contributions to the DW factor. For an atom whose equilibrium position is a centre of inversion symmetry the DW factor can be written (Wolfe & Goodman, 1969).

$$e^{-M}=\langle\exp(i\mathbf{Q}\,.\,\mathbf{u})\rangle=\exp\{-\tfrac{1}{2}\langle(\mathbf{Q}\,.\,\mathbf{u})^2 \\ +\tfrac{1}{24}[\langle(\mathbf{Q}\,.\,\mathbf{u})^4\rangle-3\langle(\mathbf{Q}\,.\,\mathbf{u})^2\rangle^2]+O(Q^6)\} \quad (1)$$

where $\mathbf{Q}$ is the scattering vector, $\mathbf{u}$ is the atomic displacement from the equilibrium position and the angle brackets denote thermal average. In the general case one must also consider terms containing averages of odd powers of the product ($\mathbf{Q}\,.\,\mathbf{u}$). Since the basal planes in the Zn lattice are mirror planes (1) applies also to the c-axis vibrations of Zn atoms. Terms of an order higher than Q^4 have not been considered here.

Mean-square vibrational amplitude of atoms

The analysis of the temperature dependences of the integrated elastic intensities for separating Gaussian and non-Gaussian terms in the DW factor was essentially the one given by Butt & Solt (1971). The c component $\langle u_z^2\rangle$ of the mean-square vibrational amplitude of Zn atoms was obtained from the experimental data eliminating the Q^4 terms through the expression

$$\langle u_z^2\rangle_T-\langle u_z^2\rangle_{T0}=\frac{Q_H^2}{Q_{H'}^2(Q_H^2-Q_{H'}^2)}\ln\frac{R_{H'}(T_0)}{R_{H'}(T)} \\ -\frac{Q_{H'}^2}{Q_H^2(Q_H^2-Q_{H'}^2)}\ln\frac{R_H(T_0)}{R_H(T)} \quad (2)$$

where Q_H and $Q_{H'}$ are the lengths of the scattering vector for the reflexions of order H and H' respectively, T_0 indicates a reference fixed temperature and $R_H(T)$ and $R_{H'}(T)$ are the integrated intensities of the elastic peaks. Equation (2) can be easily derived from (1) by putting the integrated intensities $R_H(T)$ and $R_{H'}(T)$ proportional to the square of the DW factor e^{-M}. Values of $\langle u_z^2\rangle$ derived by expression (2) with $H=0006$, $H'=0004$ and $T_0=300$ K are plotted in Fig. 2 against temperature having assumed $\langle u_z^2\rangle_{300\,\mathrm{K}}=0{\cdot}024$ Å^2. This value, which corresponds to an X-ray Debye temperature $\Theta_z=166$ K is given in literature as a result of a computation starting from best fitting the phonon dispersion curves (De Wames *et al.* 1965) and as experimentally derived from the temperature dependence of the anomalous transmission of X-rays (Ghezzi, Merlini & Pace, 1971). The present data are in substantial agreement with those given by Skelton & Katz (1968) up to about 550 K. The temperature dependence of $\langle u_z^2\rangle$ is compared in Fig. 2 with the one given in the harmonic approximation (straight continuous line) and with the one calculated taking into account the effect of the thermal expansion on the lattice frequencies (dashed line). The continuous line was evaluated by means of a fixed X-ray Debye temperature $\Theta_z=169$ K, whereas the dashed line was evaluated from thermodynamic data by making a complementary assumption on the anisotropy of atomic motions in the Zn lattice. The calculation is given in detail in the Appendix.

The comparison between the calculated curves and the experimental data in Fig. 2 suggest that anharmonic contributions in Q^2, aside from the simple term giving the correction for thermal expansion, become important at elevated temperatures. These terms are an inherent effect of lattice anharmonicity, in the sense that they cannot be removed by a simple renormalization in the frame of a quasi-harmonic theory. As shown by Maradudin & Flinn (1963), the overall amount of anharmonic contributions in Q^2 (besides thermal expansion correction) is given by the two terms $2M_1+2M_2$ arising from the quartic and cubic terms in the lattice Hamiltonian, respectively. They are both proportional to T^2, but the sign of $2M_1+2M_2$ cannot be predicted *a priori* and a considerable amount of cancellation is possible between them. The present experiment shows that $2M_1+2M_2$ has a positive sign in Zn. Finally, the T^2 dependence of the overall Gaussian contribution to $\langle u_z^2\rangle$ has been verified by plotting against T^2 the difference between the experimental data of $\langle u_z^2\rangle$ and the values given in the harmonic approximation (see Fig. 3).

Non-Gaussian anharmonic contributions to the DW factor

If the Q^2 Gaussian terms only were appreciable, we would have

$$\ln\frac{R_H(T_0)}{R_H(T)}=\frac{Q_H^2}{Q_{H'}^2}\ln\frac{R_{H'}(T_0)}{R_{H'}(T)}\,. \tag{3}$$

Equation (3) means that the temperature dependence of the integrated intensity for the reflexion of index H can be reconstructed from the data refering to the reflexion of a different index H'. However, this possibility is clearly contradicted by the experimental data, as seen by comparing in Fig. 1 the experimental temperature dependence for the 0006 reflexion with the one calculated (dashed line) by equation (3) making use of the experimental data for the 0004 reflexion. A discrepancy as large as 40% can be observed at 620 K.

The present experimental result is in partial disagreement with those given by Skelton & Katz (1968). Though their data for the c component of the mean-square displacement of the atoms substantially agree with the present one, these authors found no evidence of non-Gaussian contributions to the DW factor. The

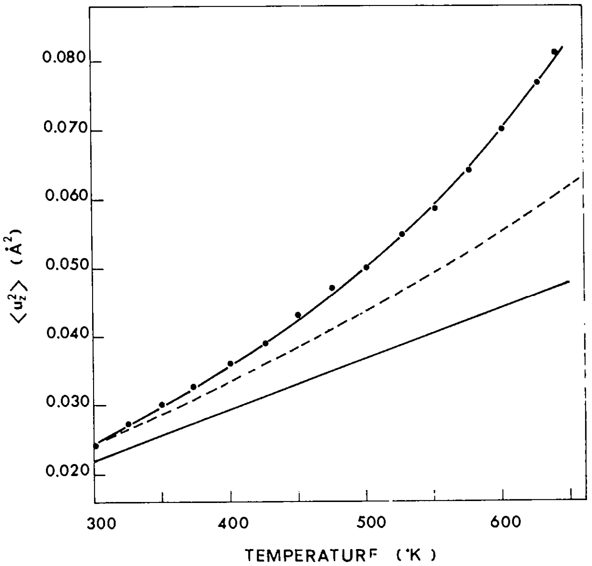

Fig. 2. Plot of the c component $\langle u_z^2\rangle$ of the mean-square atomic displacement against temperature. The continuous straight line and the dashed line give the calculated temperature dependence of $\langle u_z^2\rangle$ in the harmonic and in the quasi-harmonic approximation, respectively.

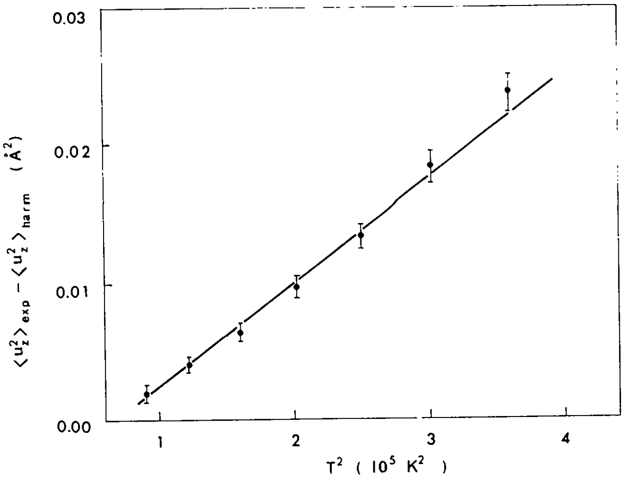

Fig. 3. Plot of $\langle u_z^2\rangle_{\mathrm{exp}}-\langle u_z^2\rangle_{\mathrm{harm}}$ as a function of T^2.

reasons for this discrepancy may be the following. (i) The data of Skelton & Katz refer to a temperature range up to about 550 K, whereas the contribution of the 'anomalous' term was found here to become significant only above 500 K (ii) Skelton & Katz measured Bragg intensities with conventional X-ray techniques after subtraction of the thermal diffuse scattering (TDS) contributions by analytical evaluation. Possible errors in the evaluation of first order and high order TDS terms may lead to considerable errors in the estimation of Bragg intensities especially when the TDS contribution is quite large. For instance, in the present experiment with a full divergence of the incident beam of 2° inelastic scattering at the 0006 peak was as much as 54% of the elastic scattering at $T=523$ K.

The amount of non-Gaussian or 'anomalous' contributions to the DW factor [for a Gaussian distribution of atomic displacements one has $\langle(\mathbf{Q}\,.\,\mathbf{u})^4\rangle=3\langle(\mathbf{Q}\,.\,\mathbf{u})^2\rangle^2$] is directly related to the experimental data by the expression

$$[\langle u_Q^4\rangle-3\langle u_Q^2\rangle^2]_{T_0}-[\langle u_Q^4\rangle-3\langle u_Q^2\rangle^2]_T=S(T_0)-S(T)$$
$$=\frac{12}{Q_H^2-Q_{H'}^2}\left[\frac{1}{Q_H^2}\ln\frac{R_H(T_0)}{R_H(T)}-\frac{1}{Q_{H'}^2}\ln\frac{R_{H'}(T_0)}{R_{H'}(T)}\right] \quad (4)$$

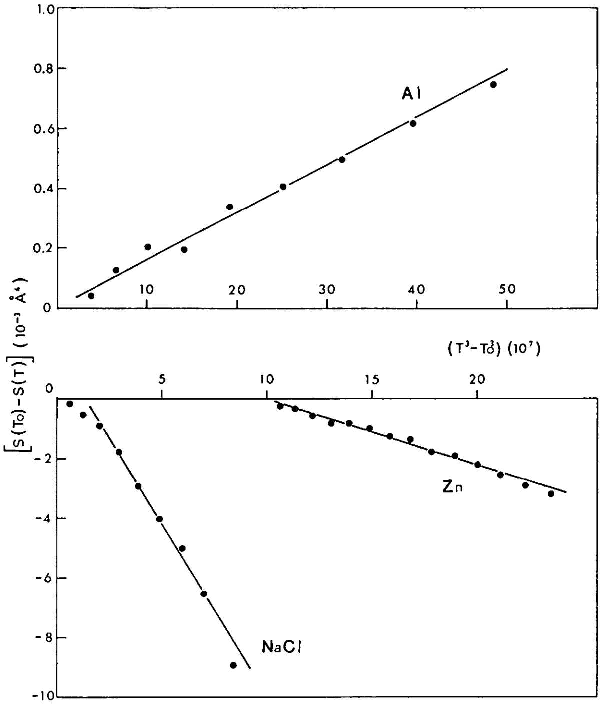

Fig. 4. Plots of the non-Gaussian term $S(T_0)-S(T)=[\langle u_Q^4\rangle-3\langle u_Q^2\rangle^2]_{T_0}-[\langle u_Q^4\rangle-3\langle u_Q^2\rangle^2]_T$ against $T^3-T_0^3$ ($T_0=300$ K) for vibrations perpendicular to basal planes in Zn and to $\{hhh\}$ and $\{h00\}$ planes in Al (Albanese & Ghezzi, 1973) and NaCl (Butt & Solt, 1971), respectively. The fact that the curve for Zn does not pass through the origin is merely an indication that non-Gaussian contributions are detectable well above room temperature (~500 K, see Fig. 1).

where u_Q is the component of the atomic displacement along the scattering vector **Q**. Values of $S(T_0)-S(T)$ for the *c*-axis vibrations in Zn with $H=0006$, $H'=0004$ and $T_0=300$ K are plotted against $T^3-T_0^3$ in Fig. 4 together with similar previously obtained results for vibrations perpendicular to $\{h00\}$ planes in NaCl (Butt & Solt, 1971) and to $\{hhh\}$ planes in Al crystals (Albanese & Ghezzi, 1973). The plots are straight lines within the experimental errors thus confirming the T^3 dependence of the Q^4 terms in the expression of M. The T^3 behaviour is quite general, as was demonstrated by Maradudin & Flinn (1963). On the other hand, the magnitude and sign of $S(T)$ depend on the particular dynamics of the crystal lattice. The exact evaluation of the anomalous term $S(T)$ is difficult because in addition to phonon frequencies and eigenvectors the coefficients of the Fourier expansions of the cubic and quartic atomic force constants must also be known. We shall therefore limit ourselves to a few qualitative comments. In addition to the fact that non-Gaussian terms were seen to be important in all the examined cases, an interesting feature of the experimental results is the sign of $S(T)$. We may distinguish two cases.

(i) *Case of* Al. We have $S(T_0)>S(T)$ for $T>T_0$. Since the absolute value of $S(T)$ increases with temperature as T^3, this means that $3\langle u_Q^2\rangle^2$ is greater than $\langle u_Q^4\rangle$. The exponential term

$$\exp\left\{\frac{Q^4}{24}[\langle u_Q^4\rangle-3\langle u_Q^2\rangle^2]\right\} \quad (5)$$

in expression (1) of the DW factor is then less than unity and it decreases with temperature as $\exp(-\alpha^2Q^4T^3)$. As a consequence of anharmonic interactions, the thermal displacements of the atoms perpendicular to the reflecting planes follow a distribution function which deviates from a Gaussian one in order to further decrease the integrated intensity of Bragg peaks.

(ii) *Case of* Zn *and* NaCl. In this case we have $S(T_0)<S(T)$ for $T>T_0$, so that $3\langle u_Q^2\rangle^2$ is smaller than $\langle u_Q^4\rangle$. The exponential (5) is greater than unity and increases with temperature as $\exp(\alpha^2Q^4T^3)$. This means that the distribution function for the atomic displacements deviates from a Gaussian one in such a way that the intensity of Bragg peaks becomes greater than if it were determined by the second moment of u_Q only.

As is known, the probability density distribution $p(\mathbf{u})$ of an atom, also known as the thermal smearing function, can be found by Fourier transform of the DW factor $\exp[-M(\mathbf{Q})]$ (see, for example, Willis & Pryor, 1975). As an example, some smearing functions were calculated for Al ($T=800$ K) and for Zn ($T=640$ K). The results are plotted in Fig. 5. In the Al case, u is the displacement of an atom parallel to $\langle 111\rangle$ directions. The experimental data of Albanese & Ghezzi (1973) were used. Two functions $p(u)$ of Gaussian shape were calculated; the first (*a*) based on the value for $\langle u^2\rangle$ obtained by extrapolating at $T=800$

K in the harmonic approximation the low-temperature data, the second (*b*) using the experimental value of $\langle u^2\rangle$ at $T=800$ K but assuming a vanishing contribution of the Q^4 term. A third function (*c*) (dashed line) was obtained by taking into account the non-Gaussian Q^4 term: this is the one consistent with the experimental data. The deviations between (*b*) and (*c*) smearing functions are entirely due to the presence of the Q^4 anomalous term. Similar calculations were performed for Zn at $T=640$ K. In this case u is the thermal displacement of an atom parallel to the c axis. Moreover, owing to the positive sign of the argument of the exponential (5), a negative Q^6 term was inserted in the calculation to make the integral

$$\int_0^\infty \exp\,[-M(Q)]\cos\,(uQ)\mathrm{d}Q$$

convergent. The magnitude of the Q^6 term was chosen to affect the elastic intensity data of the 0006 reflexion at $T=640$ K by at most 5%.

As far as we are concerned in the case of Zn and NaCl, it is not clear at present if the fact that $S(T_0)<S(T)$ may be understood through simple considerations of the lattice dynamics of these crystals. We may notice that the available experimental data are related only with atomic motions perpendicular to lattice planes of easy cleavage [$\{h00\}$ planes in NaCl and basal planes in Zn]. As suggested by Borgonovi, Caglioti & Antal (1963), the structure of basal planes in Zn preserves a strong individuality within the crystal so that one may believe that the manner in which the lattice breaks up upon melting can be analogous to a sequence of successive detachments of layer building units. It would be interesting to investigate if there were some relation between this behaviour of the lattice planes and the anomalous 'increase' of Bragg reflexions, expecially when high-temperature Mössbauer measurements of DW factors in different crystal directions will be available.

4. Conclusions

The integrated intensities for Bragg scattering were measured at the 0002, 0004 and 0006 reflexions of a Zn single crystal in the temperature range 295–640 K. The Mössbauer technique was used to measure the purely elastic scattering without any contributions of Compton and phonon scattering. The DW factor for the c component of the atomic motions was found to be considerably affected by the presence of anharmonic non-Gaussian or 'anomalous' Q^4 terms. The overall magnitude of the anomalous term was derived by comparing the experimental temperature dependence of Bragg scattering with the one for an ideally mosaic crystal. The T^3 dependence of $\langle u_z^4\rangle-3\langle u_z^2\rangle^2$ was verified and it was proved that $\langle u_z^4\rangle$ is greater than $3\langle u_z^2\rangle^2$, so that the intensity of Bragg peaks is greater than if it were controlled by the second moment of u_z only. This result was compared with those previously obtained for NaCl and Al crystals.

The c component $\langle u_z^2\rangle$ of the mean-square vibrational amplitude of the atoms was obtained as a function of temperature from the experimental data. The comparison of the temperature dependence of $\langle u_z^2\rangle$ with the calculated dependence in the quasi-harmonic approximation suggested the presence of important contributions proportional to Q^2 and T^2, with an overall positive sign, which are inherent effects of lattice anharmonicity.

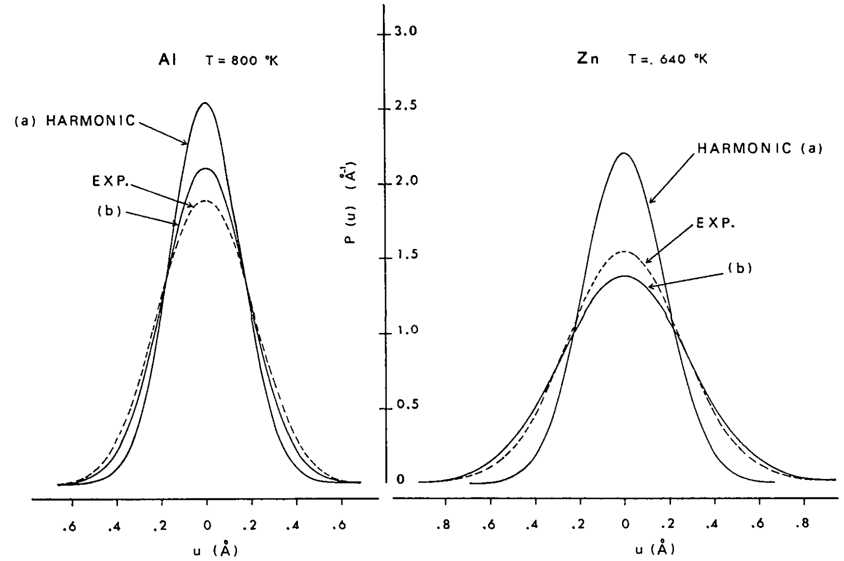

Fig. 5. Calculated thermal smearing functions $p(u)$ of the atoms for Al ($T=800$K, $\langle 111\rangle$ direction) and Zn ($T=640$K, c axis). Curves (*a*) are based on the harmonic approximation. Curves (*b*) consider purely Gaussian anharmonic contributions. Curves (*c*) are consistent with the experimental data [Albanese & Ghezzi (1973) for Al; present work for Zn].

APPENDIX

Owing to the anisotropy of the hexagonal lattice, the thermal expansion correction for the DW factor does not follow directly from the definition of the Grüneisen parameter, as in cubic crystals. We may start with the definition of $\langle u^2\rangle$, the average value of the mean-square displacement in all crystal directions as

$$3\langle u^2\rangle = 2\langle u_x^2\rangle + \langle u_z^2\rangle\,. \tag{6}$$

$\langle u_x^2\rangle$ and $\langle u_z^2\rangle$ define the directional X-ray Debye temperatures Θ_x and Θ_z through the expression

$$\langle u^2_{x(z)}\rangle = \frac{3\hbar^2 T}{m K_B \Theta^2_{x(z)}} \tag{7}$$

which is valid in the classical limit. Equations (6) and (7) define an isotropic X-ray Debye temperature Θ which is related to Θ_x and Θ_z by

$$\frac{3}{\Theta^2} = \frac{2}{\Theta_x^2} + \frac{1}{\Theta_z^2}\,. \tag{8}$$

Owing to lattice expansion Θ varies with temperature as

$$\frac{\Theta_0}{\Theta} = \left(\frac{a}{a_0}\right)^{2\gamma_x(-2)} \left(\frac{c}{c_0}\right)^{\gamma_z(-2)} \tag{9}$$

where a and c are the lattice constants, the subscript 0 refers to a particular fixed temperature T_0 and the Grüneisen parameters $\gamma_x(-2)$ and $\gamma_z(-2)$ are defined by the general formula (15) in the paper of Barron & Munn (1966). The particular index (-2) appears owing to the proportionality between $1/\Theta^2$ and the inverse squares of the lattice frequencies. Equations (8) and (9), together with the expression (7), are not enough to calculate the temperature dependence of $\langle u_x^2\rangle$ and $\langle u_z^2\rangle$ separately. A complementary equation must be assumed which signifies a physical hypothesis. To do this, Barron & Munn (1967) suggested that $\langle u_z^2\rangle$ was affected only by expansion along the hexagonal axis, and that this was also true for $\langle u_x^2\rangle$. However, the correct Grüneisen parameters for this approximation are not $\gamma_x(-2)$ and $\gamma_z(-2)$ but we need new parameters which account for the strain dependence of only those phonon modes giving non-vanishing contributions to the atomic displacements parallel or perpendicular to the c axis. Since these latter quantities cannot be found as thermodynamic data, we introduced the simpler approximation that the ratio $\langle u_z^2\rangle/\langle u_x^2\rangle$ should be kept proportional to $(c/a)^2$ with varying temperature. The equivalent condition for Θ_x and Θ_z is

$$\frac{\Theta_x^0 a_0}{\Theta_x a} = \frac{\Theta_z^0 c_0}{\Theta_z c}\,. \tag{10}$$

In other words, we assume that in the quasi-harmonic approximation the ratio $\langle u_z^2\rangle/\langle u_x^2\rangle$ changes with temperature only as a consequence of variations in the anisotropy of the unit cell. The fact that the experimental ratio $\langle u_z^2\rangle/\langle u_x^2\rangle$ increases faster than $(c/a)^2$ especially in the high temperature range [see the experimental data of Skelton & Katz (1968) and the thermal expansion data] does not contradict our hypothesis and it may be assumed to be an inherent effect of lattice anharmonicity.

The quasi-harmonic temperature dependence of $\langle u_z^2\rangle$ was then calculated through equations (8), (9) and (10), together with expression (7) and the X-ray Debye temperature $\Theta_x^0 = 254$ K, $\Theta_z^0 = 169$ K (Skelton & Katz, 1968) and $\Theta_0 = 213$ K for $T_0 = 100$ K. This value for the reference temperature T_0 was chosen since for $T \le 100$ K the available data in the literature do not indicate significant anharmonic contributions to $\langle u_x^2\rangle$ and $\langle u_z^2\rangle$. Finally, we used the values $\gamma_x(-2) = 1{\cdot}65$ and $\gamma_z(-2) = 2{\cdot}77$ (Barron & Munn, 1966) for the Grüneisen parameters, the high-temperature thermal expansion data of Owen & Yates (1934) and the low temperature ones of Meyerhoff & Smith (1962).

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