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Examination of the Thermal Variation of the Mean Square Atomic Displacements in Zinc and Evaluation of the Associated Debye Temperature[*][†]

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The two principal components of the mean square atomic displacement differences due to thermal vibrations in zinc have been measured from single-crystal x-ray diffraction intensities over a thermal range from 4.85 to 600°K. The absolute value of the components of the mean square atomic displacements parallel to the hexagonal axis and lying in the basal plane have been evaluated from the data by means of a self-consistent technique; these mean square atomic displacements are compared with existing theoretical and experimental values. The x-ray Debye temperatures $\Theta^M(T)$ have been evaluated; $\Theta^M(0)$ is found to be 219.6°K, whereas $\Theta^M(600)$ drops to 187°K. The values of $\Theta^M(T)$ are compared with theoretical calculations, as well as with other experimental results. The thermal variation of $\Theta^M(T)$ appears to be explained by volume-expansion effects over a limited thermal range ($100°\mathrm{K}<T<400°\mathrm{K}$). At higher temperatures, additional anharmonic effects appear to be present. An analysis of measured and calculated values of the temperature derivative of the mean square displacement has led to an evaluation of constant-volume anharmonic effects. Comparison is also made between $\Theta^M(T)$ and Debye temperatures relating to other averages over the frequency-distribution function.

I. INTRODUCTION

THE thermal vibrations of the atoms in a crystalline solid can be investigated through a study of the x-ray intensity scattered into a Bragg diffraction peak. The mean square atomic vibrations can be related to an average over the frequency spectrum and represented in terms of a characteristic or Debye temperature. Herbstein[1] has reviewed the various methods of evaluating Debye temperatures and discussed the interrelations between different techniques of measurement.

In general, the x-ray Debye temperature $\Theta^M(T)$ is expressed in terms of a summation of the principal atomic mean square displacements over all the atoms in a primitive cell. For a hexagonal lattice with two similar atoms per unit cell, $\Theta^M(T)$ can be related to the sum of the component of the mean square atomic displacements parallel to the hexagonal axis $\langle u_z^2\rangle_T$ and of the average displacements corresponding to the components of the thermal vibrations in the basal plane $\langle u_x^2\rangle_T$.[2] A study of the components of the mean square displacement in these two principal directions also provides a measure of the anisotropy of the system. An examination of the absolute value and of the thermal variation of the x-ray Debye temperature provides a convenient means of comparison between experiment and lattice-dynamical force-model calculations. Furthermore, a comparison between $\Theta^M(T)$ and other experimentally determined Debye temperatures, e.g., specific heats $[\Theta^C(T)]$, elastic constants $[\Theta^E(T)]$, and electrical resistivities $[\Theta^R(T)]$, often yields information about the frequency-distribution function.

II. THEORY

The intensity of a general Bragg reflection scattered from a mosaic, hexagonal crystal containing two similar atoms per primitive cell can be expressed, at a given temperature T, in the following form:

$$\langle I_{\text{meas.}}(\mathbf{S}/\lambda,T)\rangle = C|F|^2 I_0(\mathbf{S}/\lambda) \times\exp[-2M_{\mathrm{S}_z}(T)\cos^2\psi-2M_{\mathrm{S}_x}(T)\sin^2\psi] + \sum_{j=1}^{\infty} I_{\mathrm{TDS}-j}(\mathbf{S}/\lambda,T), \quad (1)$$

where C is a constant, F is the structure factor, $I_0(\mathbf{S}/\lambda)$ is the Laue interference function, $\mathbf{S}$ is the diffraction vector, λ is the wavelength of the x radiation, and ψ is the angle between the hexagonal axis and $\mathbf{S}$. The exponential function in Eq. (1) is commonly referred to as the Debye-Waller factor; the terms in the Debye-Waller factor are related, within the quasiharmonic approximation, to the components of the mean square atomic displacement in the following fashion:

$$2M_{\mathrm{S}_p}(T)=(4\pi\sin\theta/\lambda)^2\langle u_p^2\rangle_T;\quad p=z \text{ or } x, \quad (2)$$

where θ represents the Bragg diffraction angle, $\langle u_z^2\rangle_T$ denotes the component of the mean square displacement parallel to the hexagonal axis, and $\langle u_x^2\rangle_T$ refers to the projection of the mean square displacement onto the basal plane.

The series of terms on the right-hand side of Eq. (1)

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[1] F. H. Herbstein, Advan. Phys. **10**, 313 (1960).

[2] M. Blackman, Acta Cryst. **9**, 734 (1956).

represents the thermal diffuse scattering (hereafter referred to as TDS). $I_{\mathrm{TDS}-j}(\mathbf{S}/\lambda,T)$ denotes the jth order TDS, i.e., it represents the interaction between an incident x-ray photon and j phonons. The TDS will tend to increase with increasing temperatures. In order to account for this, the TDS contribution is analytically evaluated and subtracted from the measured intensity. The two basic assumptions involved in this calculation are (1) that optical mode contributions to the measured TDS will be accounted for in the background correction and (2) that any possible dispersion effects can be neglected in evaluating the contribution from the acoustical modes. These approximations are presumed to be justified by the fact that the region of interest in reciprocal space is small in comparison to the volume of the Brillouin zone. In addition, if ψ is restricted to values of 0° or 90°, Eq. (1) can be rewritten in terms of only one principal component of the atomic displacement as follows:

$$\langle I_{\mathrm{meas}}(\mathbf{S}/\lambda,T)\rangle=C|F|^2I_0(\mathbf{S}/\lambda)e^{-2M_{\mathbf{S}}(T)},\qquad(3)$$

where it is understood that $\mathbf{S}$ now refers to a principal direction.

Since it is rather difficult to evaluate the absolute value of the multiplicative constants in Eq. (3), it is common practice to consider intensity ratios, usually referred to some arbitrary reference temperature, T_0.[3–5] Evaluation of the intensity ratio, with the aid of Eq. (2) yields the following expression:

$$\langle u_p^2\rangle_T-\langle u_p^2\rangle_{T_0}=(\lambda/4\pi\sin\theta)^2\times\ln[Q_p(T)/Q_p(T_0)]=R_p(T),\quad p=x\text{ or }z\qquad(4)$$

where $Q(T)$ represents the measured intensity corrected for background contributions, TDS, and for the small effects due to thermal expansion.

For the aforementioned hexagonal system, the atomic mean square displacements can be related to the frequency-distribution function $g(\nu)d\nu$ in the following fashion:

$$3\langle u^2\rangle_T=\langle u_z^2\rangle_T+2\langle u_x^2\rangle_T=\frac{3}{4\pi^2m}\int_{\nu=0}^{\nu_{\max}}\frac{1}{\nu^2}\left[\tfrac{1}{2}h\nu+\frac{h\nu}{e^{h\nu/kT}-1}\right]g(\nu)d\nu\Bigg/\int_{\nu=0}^{\nu_{\max}}g(\nu)d\nu,\qquad(5)$$

where m is the atomic mass, ν is the lattice frequency, and h and k have their usual meaning. If the Debye spectrum is employed in Eq. (5), the following familiar relation is obtained:

$$3\langle u^2\rangle_T=\langle u_z^2\rangle_T+2\langle u_x^2\rangle_T=\frac{9h^2}{4\pi^2mk\Theta^M(T)}\left[\frac{\Phi(\chi_T)}{\chi_T}+\frac{1}{4}\right],\qquad(6)$$

where

$$\Phi(\chi_T)=\frac{1}{\chi_T}\int_{\xi=0}^{\chi_T}\frac{\xi}{e^\xi-1}d\xi;\quad\chi_T=\Theta^M(T)/T.\qquad(7)$$

A source of difficulty in the evaluation of the mean square displacements, and hence of the x-ray Debye temperature, lies in the determination of the reference values $\langle u_{z,x}^2\rangle_{T_0}$. Several techniques for solving the similar problem for cubic systems have been proposed in the literature.[4–7] We have extended two of these procedures, the low-temperature approximation of Flinn *et al.*[5] and the derivative technique of Nicklow and Young,[7] to this hexagonal system.

A. Low-Temperature Approximation

Although it is indeed possible to work with the mean square displacement $\langle u^2\rangle_T$, it is more profitable to consider its two principal components. As an artifice, the "directional Debye temperature," originally proposed by Grüneisen and Goens[8] and later employed by Brindley,[9] is introduced. In essence, for an anisotropic system, a directional Debye temperature is associated with the component of the mean square displacement in a given direction, as if the system were isotropic, and all atoms vibrated with the particular component of the mean square displacement associated with that direction, i.e.,

$$\langle u_p^2\rangle_T=\frac{3h^2}{4\pi^2mk\Theta_p^M(T)}\left[\frac{\Phi(\chi_{T,p})}{\chi_{T,p}}+\frac{1}{4}\right],\quad p=x\text{ or }z\qquad(8)$$

where $\chi_{T,p}$ and $\Phi(\chi_{T,p})$ are similar to the expressions given in Eq. (7).

If Eq. (8) is substituted in Eq. (4), the following relation is obtained:

$$-\frac{3h^2}{4\pi^2mk}\left[\frac{\Phi(\chi_{T_0,p})}{\chi_{T_0,p}^2T_0}-\frac{\Phi(\chi_{T,p})}{\chi_{T,p}^2T}+\frac{1}{4}\left(\frac{1}{\chi_{T_0,p}T_0}-\frac{1}{\chi_{T,p}T}\right)\right]=R_p(T).\qquad(9)$$

Now, as argued by Flinn *et al.*,[5] if T is significantly smaller than $\Theta^M(T_0)$, $\Theta^M(T)$, and T_0, then the second two terms on the left-hand side in Eq. (9) are negligible in comparison to the first term, e.g., in the worst case for Zn, with $T_0=300$°K and $T=4.85$°K, the second and third terms represent less than 0.1 and 1.5% of the first term, respectively. For such cases, Eq. (9) takes the following approximate form:

$$-\frac{3h^2}{4\pi^2mk}\left[\frac{\Phi(\chi_{T_0,p})}{\chi_{T_0,p}^2T_0}\right]\approx R_p(T)\qquad(10)$$

Thus, with sufficiently low-temperature data, absolute

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[3] A. Paskin, Acta Cryst. **10**, 667 (1957).

[4] D. R. Chipman, J. Appl. Phys. **31**, 2012 (1960).

[5] P. A. Flinn, G. M. McManus, and J. A. Rayne, Phys. Rev. **123**, 809 (1961).

[6] K. Alexopoulos, J. Boskovits, S. Mourikis, and M. Roilos, Acta Cryst. **19**, 349 (1965).

[7] R. M. Nicklow and R. A. Young, Phys. Rev. **152**, 591 (1966).

[8] E. Grüneisen and E. Goens, Z. Physik **29**, 141 (1924).

[9] G. W. Brindley, Phil. Mag. **21**, 790 (1936).

values of $\langle u_{z,x}^2\rangle_{T_0}$ can be evaluated and, hence, the mean square displacements at all other temperatures can be determined from Eq. (4).

B. Derivative Technique

As previously noted, the second procedure for evaluating the absolute value of the Debye temperature from the measured mean square displacement differences involves extension of the derivative technique of Nicklow and Young.[7] The basic assumption of this procedure is that the thermal variation of the lattice frequencies can be attributed to thermal expansion effects only. For a hexagonal system, the full derivative of the mean square displacement is then given by the following:

$$\langle u^2\rangle'_T=\frac{d\langle u^2\rangle_T}{dT}=\left(\frac{\partial\langle u^2\rangle_T}{\partial T}\right)_{a,c}+\left[\left(\frac{\partial\langle u^2\rangle_T}{\partial a}\right)_{c,T}\frac{\partial a}{\partial T}+\left(\frac{\partial\langle u^2\rangle_T}{\partial c}\right)_{a,T}\frac{\partial c}{\partial T}\right]. \tag{11}$$

The partial derivatives on the right-hand side of Eq. (11) can be evaluated in a manner similar to that detailed in the aforementioned reference.[7] This evaluation, in conjunction with the Debye frequency-distribution function, leads to the following expression:

$$\langle u^2\rangle'_T=\frac{3h^2}{4\pi^2mkT^2}\frac{1}{\chi^2}\left[f(\chi)+\left\{T[\gamma_c(-2)\alpha_c+2\gamma_a(-2)\alpha_a]\times\left(\chi\left[\frac{\Phi(\chi)}{\chi}+\frac{1}{4}\right]+f(\chi)\right)\right\}\right], \tag{12}$$

where

$$f(\chi)\equiv\frac{1}{\chi}\int_{\xi=0}^{\chi}\frac{\xi^2e^\xi}{(e^\xi-1)^2}d\xi. \tag{13}$$

α_c and α_a are the coefficients of linear expansion parallel and perpendicular to the hexagonal axis, respectively; $\gamma_c(-2)$ and $\gamma_a(-2)$ are the Grüneisen parameters related to the inverse-second moment of the frequency distribution for a hexagonal system as defined by Barron and Munn.[10] It should be noted that in evaluating the second term on the right-hand side in Eq. (11), it was assumed that $T\geq\Theta^M(T)$. Thus, strictly speaking, Eq. (11) is only applicable in this high-temperature region. The left-hand side of Eq. (12) represents the sum of the temperature derivatives of the principal mean square displacements and can be evaluated directly at any given temperature. The right-hand side of Eq. (12) can then be varied until a fit is determined and a Debye temperature thus evaluated. Since the function contained in this averaging expression is slightly different from that used in Eq. (6), the Debye temperature obtained from Eq. (12) will not necessarily be equivalent to the Debye-Waller Debye temperature; it is therefore denoted by $\Theta^{M'}(T)$.

Additional physical significance can be attributed to the temperature derivative of the mean square displacement if one realizes that, in this temperature region, the mean square displacement can be expressed in the following approximate form:

$$\langle u^2\rangle_T\approx(3h^2/4\pi^2mk)[T/\Theta^M(T)^2]. \tag{14}$$

Thus, the degree to which a plot of $\langle u^2\rangle'_T$ versus temperature departs from a horizontal line represents a measure of the thermal variation of $\Theta^M(T)$.

III. EXPERIMENTAL PROCEDURE

Three different zinc single crystals, grown from 99.999% pure zinc, were used in this investigation. The samples were irradiated with filtered radiation from a molybdenum x-ray tube; the diffracted radiation was measured with a proportional counter in conjunction with an electronic pulse-height discriminator. The method of measuring the integrated intensities is similar to that described previously.[11] In order to detect any possible thermal fluctuations in the measured intensities due to possible variation of the extinction or absorption effects, e.g., due to possible shifting of the mosaic blocks, several reflections were studied, viz., the (004), (006), and (008) reflections for the parallel data and the (300), (400), (600), and (210) for the data corresponding to thermal vibrations in the basal plane.

The low-temperature data were obtained using an automatically controlled cryogenic x-ray system manufactured by Electronics and Alloys, Inc. The temperature control and measurement are believed to be accurate to within ±0.2°K. High temperatures were achieved by means of focused heating lamps and measured in the manner described previously.[11]

IV. RESULTS AND DISCUSSION

A. Mean Square Displacements

The basic experimental results of this investigation are the components of the mean square displacement differences in the two principal directions for zinc. Use of the low-temperature measurements in Eq. (10) leads to the following values for the two principal mean square displacement components at the reference temperature 300°K: $\langle u_z^2\rangle=0.0259\pm0.001$ Å^2; $\langle u_x^2\rangle=0.0112\pm0.0003$ Å^2. Utilizing these results, the data can be plotted on an absolute scale; the components of the mean square displacement in the two principal directions are shown in Fig. 1. The smooth curves running through the data represent least-square curve fits.

Using thermodynamic data, Barron and Munn[12] evaluated the mean square displacement $\langle u^2\rangle_T$ for zinc. Then, using the lattice dynamical force model of

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[10] T. H. K. Barron and R. W. Munn, Phil. Mag. **15**, 85 (1967).

[11] R. H. Wilson, E. F. Skelton, and J. L. Katz, Acta Cryst. **21**, 635 (1966).

[12] T. H. K. Barron and R. W. Munn, Acta Cryst. **22**, 170 (1967)

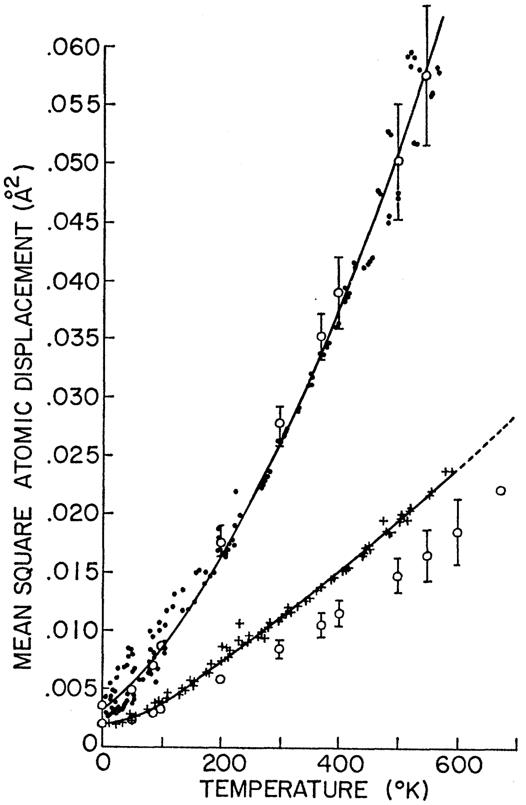

FIG. 1. Components of the mean square atomic displacement of zinc parallel to the hexagonal axis (●) and lying in the basal plane (+). The calculations by Barron and Munn (Ref. 12) are shown in circles.

DeWames *et al.*,[13] and an approximation for thermal expansion effects, they calculated $\langle u_x{}^2\rangle_T$. Finally, $\langle u_z{}^2\rangle_T$ was found by taking the difference between $\langle u_z{}^2\rangle_T$ and $2\langle u_x{}^2\rangle_T$. The results of their calculations for $\langle u_z{}^2\rangle_T$ and $\langle u_x{}^2\rangle_T$ are shown in Fig. 1. The agreement between the measured values and these calculated mean square displacement components appears to be rather good in the low-temperature region ($4.85 \leq T < 100$°K). Further, the agreement between theory and experiment appears to be quite good over the whole thermal range ($4.85 < T < 600$°K) for the components of the thermal vibrations parallel to the hexagonal axis. The measured values of $\langle u_x{}^2\rangle_T$, on the other hand, show a discrepancy with the calculated values which appears to increase with increasing temperature; at 600°K, this difference amounts to about 25% of the measured value. It is indeed possible that this high-temperature discrepancy in $\langle u_x{}^2\rangle_T$ may be caused by constant-volume anharmonic effects.

B. X-Ray Debye Temperatures

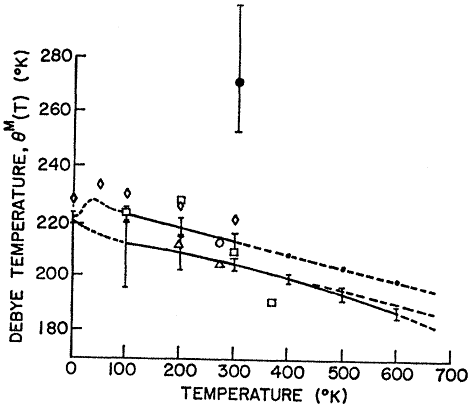

FIG. 2. Debye temperature of zinc experimentally determined by x-ray techniques (lower curve) and calculated by Barron and Munn (Ref. 12) (upper curve). □: measured by Jauncey and Bruce (Ref. 14); ◇: calculated from the DeWames *et al.* force model (Ref. 13); ○: calculated from electrical conductivity by Weisskopf (Ref. 16); △: calculated from electrical conductivity data of Pawlek and Rogalla (Ref. 17); ●: measured by Kündig *et al.* (Ref. 18) from Mössbauer experiments.

Combining these mean square displacement components as indicated in Eq. (6) leads to immediate evaluation of the x-ray Debye temperatures. These results are shown in Fig. 2, along with other measurements and calculations of the equivalent Debye temperature $\Theta^M(T)$. The error bars reflect the scatter in the data, as seen in Fig. 1. In the low-temperature region ($T < 100$°K) the Debye function is extremely sensitive to the scatter in the data; the errors associated with the calculated values of $\Theta^M(T)$ in this region would be inordinately large. Therefore, the $\Theta^M(T)$-T curve is shown dashed below 100°K; the true shape of the curve cannot be accurately evaluated from the data in this region. It is interesting to note, however, that the value of $\Theta^M(0)$ extrapolated from 4.85°K is 219.6°K; as expected from the mean square displacements, this is in excellent agreement with the Barron and Munn[12] calculated value of 221±2°K.

The high-temperature thermal variation of the calculated value of $\Theta^M(T)$ is based on thermal expansion effects only. Clearly, the effects of volume expansion can adequately explain the shape of the measured $\Theta^M(T)$-T curve over a rather broad thermal range ($100 < T < 400$°K). Above 400°K, however, the measured Debye temperature appears to drop more rapidly with increasing temperature than predicted by lattice expansion effects alone. At 600°K, this drop represents about 16% of the effect due to thermal expansion. It is assumed that the increased slope of the $\Theta^M(T)$-T curve above 400°K is caused by constant-volume anharmonic effects. Not being aware of any theoretical examination of the effects of these anharmonic contributions to $\Theta^M(T)$, it is difficult to test the foregoing assumption. (Maradudin and Flinn[14] have examined cubic and quartic anharmonic contributions to the Debye-Waller factor of cubic materials.) Suffice it to say

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[13] R. E. DeWames, T. Wolfram, and G. W. Lehman, Phys. Rev. **138**, A717 (1965).

[14] A. A. Maradudin and P. A. Flinn, Phys. Rev. **129**, 2529 (1963).

that this behavior of $\Theta^M(T)$ for zinc is similar to the effects seen in Ag and Pb as reported by Alexopoulos *et al.*,[6] and in Al, Pb, and β-brass as reported by Chipman.[4] Furthermore, the size of this apparent constant-volume anharmonic contribution is in keeping with what might be expected for zinc.[12]

The measurements of $\Theta^M(T)$ made by Jauncey and Bruce[15] from diffuse scattering of x rays are shown in Fig. 2. Realizing that this pioneer work was carried out with film techniques, the limited agreement seen is gratifying.

Also plotted in Fig. 2 are the calculations of $\Theta^M(T)$ from the DeWames *et al.*[13] modified axially symmetric force model and corrected for thermal expansion by Barron and Munn.[12] The results of the model calculation are consistently about 8% higher than the measurements of this work. In consideration of the apparently large value of $\Theta^M(T)$ calculated from the DeWames *et al.* model,[13] Barron and Munn[12] have suggested that the model, like many short-range force models for Zn, does not adequately account for the large dispersion effects seen in the acoustical lattice waves propagating in the basal plane with atoms vibrating normal to the plane, as measured from coherent inelastic neutron scattering data. Rather, the model tends to overestimate these frequencies and hence leads to an excessive value of $\Theta^M(T)$.

It is interesting to compare these results with other calculations of the equivalent Debye temperature. In the high-temperature region, the electrical conductivity of metals can be related to the mean square displacement and hence to an equivalent Debye temperature $\Theta^R(T)$. Although it is understood that to calculate $\Theta^R(T)$ from the electrical conductivity is rather difficult to perform exactly, approximate results can be obtained using the expressions of Weisskopf[16] in conjunction with the electrical resistivity data of Pawlek and Rogalla.[17] These results are shown on Fig. 2, and, in the light of the approximations involved, appear to show surprisingly good agreement with the results of this work.

Kündig *et al.*[18] have evaluated the two directional Debye temperatures for zinc from the Mössbauer effect of Fe^{57} in Zn. Averaging their directional Debye temperatures yields $\Theta^M(296)=273_{-19}^{+29}$°K; this appears to be in serious disagreement with the results of this work. From this discrepancy one might infer that their basic assumption, that "the force constants for the Fe impurity atoms in Zn are about the same as for the Zn atoms,"[18] is in serious question. {*Note added in proof.* This apparently high value of $\theta^M(296)$ tends to suggest that the binding forces between the Fe and Zn atoms are somewhat stronger than the binding forces between the Zn atoms themselves. As pointed out to us by Dr. Nussbaum, this conclusion is consistent with his Mössbauer measurements on Zn [R. M. Housley and R. H. Nussbaum, Phys. Rev. **138**, A753 (1965)]}.

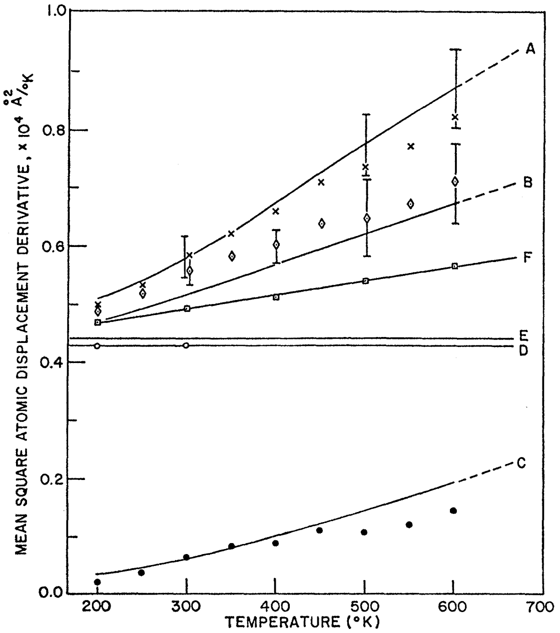

FIG. 3. Thermal variation of mean square displacement derivatives. Curve A: $\langle u^2\rangle'_T$ measured; curve B: $(\partial<u^2\rangle_T/\partial T)_{aT,cT}$ calculated; curve C: $[(\partial\langle u^2\rangle_T/\partial a)_{c,T}\partial a/\partial T+(\partial\langle u^2\rangle_T/\partial c)_{a,T}\partial c/\partial T]$ calculated; curve D: $(\partial\langle u^2\rangle_T/\partial T)_{a0,c0}$ calculated from DeWames *et al.* (Ref. 13) force model; curve E: $(\partial\langle u^2\rangle_T/\partial T)_{a0,c0}$ determined from Barron and Munn (Ref. 12) calculation; curve F: $(\partial\langle u^2\rangle_T/\partial T)_{aT,cT}$ determined from Barron and Munn (Ref. 12) calculation. ◇: $\langle u^2\rangle'_T$ determined from Barron and Munn (Ref. 12) calculation; ●: $[(\partial\langle u^2\rangle_T/\partial a)_{c,T}\partial a/\partial T+(\partial\langle u^2\rangle_T/\partial c)_{a,T}\partial c/\partial T]$ determined from Barron and Munn (Ref. 12) calculation; ×: $\langle u^2\rangle'_T$ calculated from Barron and Munn (Ref. 12) and corrected for constant-volume anharmonic effects.

C. Mean Square Displacement Derivatives

As mentioned earlier, the fundamental measurements obtained from this experiment are the mean square atomic displacement differences. Since we can separate the implicit temperature dependence of $\langle u^2\rangle'_T$ into its constituent parts, within the quasiharmonic approximation, it is interesting to examine the slopes of the average atomic displacement. Curve A in Fig. 3 represents the combined, measured slopes of the two principal components of the mean square displacements for $T>200$°K, since the theoretical development is only valid for $T\geq\Theta^M(T)$. Using these data in Eq. (12), an effective Debye temperature $\Theta^{M'}(T)$ is calculated; these results are shown in Fig. 4. Once the values of $\Theta^{M'}(T)$ are known, one can return to Eqs. (11) and (12) and evaluate the separate influences of temperature and lattice expansion on the average displacement slopes. In Fig. 3, curve B represents the explicit thermal effect, i.e., $(\partial\langle u^2\rangle_T/\partial T)_{a_T c_T}$; curve C shows the calculated effects of thermal expansion. Clearly the explicit effects of lattice

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[15] G. E. M. Jauncey and W. A. Bruce, Phys. Rev. **51**, 1067 (1937).

[16] V. F. Weisskopf, Am. J. Phys. **11**, 1 (1943).

[17] F. Pawlek and D. Rogalla, Cryogenics **6**, 14 (1966).

[18] W. Kündig, K. Ando, and H. Bömmel, Phys. Rev. **139**, A889 (1965).

expansion become significantly more important at higher temperatures; at 200°K they represent less than 8% of $\langle u^2\rangle'_{200}$ whereas, at 600°K, about 22% of $\langle u^2\rangle'_{600}$ is attributable to explicit thermal expansion effects.

The values of $\langle u^2\rangle'_T$ and the two partial derivatives determined from the calculations of Barron and Munn[12] are also shown in Fig. 3. In the intermediate temperature range ($200\leq T\leq 300$) there appears to be limited agreement, within experimental error, between the measured values of $\langle u^2\rangle'_T$ and the equivalent values taken from the Barron and Munn work. However, at higher temperatures ($T\geq 300$°K), where anharmonic effects become more important, the measured and calculated results appear to differ by up to 18%.

Curve F represents the explicit constant-volume thermal influence on the average displacement slopes, as a function of temperature, i.e., $(\partial\langle u^2\rangle_T/\partial T)_{a_Tc_T}$ as determined from the reported values of Barron and Munn.[12] This is distinctly different from the thermal variation and magnitude of the slope that one would expect if the lattice cell lengths were fixed at their 0°K value, i.e., $(\partial\langle u^2\rangle_T/\partial T)_{a_0c_0}$. This latter effect, as calculated from the specific heat data,[12] is shown in curve E; the value of $(\partial\langle u^2\rangle_T/\partial T)_{a_{298}c_{298}}$, determined from the DeWames *et al.*[13] force model, is shown in curve D. Clearly, these calculations indicate that if the crystal exhibited no thermal expansion at all, the mean square displacement would increase linearly with increasing temperature. Thus, the region between curves E and F indicates (1) that the thermal influence on the mean square displacements will cause an increase in $\langle u^2\rangle_T$ above that predicted by the explicit temperature effect at a_0 and c_0, because the lattice parameters have expanded; and (2) that this additional effect of the expanded lattice tends to increase with increasing temperature. Curves D and E correspond to a thermally invarient Debye temperature and the effect of the expanded lattice discussed above will tend to cause a drop in this Debye temperature, which increases with increasing temperature.

The explicit influence of the lattice expansion on the atomic displacements, as calculated from the Barron and Munn[12] results, appears to show good agreement with the results evaluated here (curve C); the small discrepancy seen may well be due to the experimental error involved in evaluating $\langle u^2\rangle'_T$.

Taking this as a check on curve C, we attempt to explain the difference between curves B and F. In the analysis used to separate the measured values of $\langle u^2\rangle'_T$ (curve A) into the two components (curves B and C) it was assumed that the thermal variation of the phonon frequencies was due to lattice expansion effects only, i.e., any possible constant-volume anharmonic effects that might contribute to the measured values of $\langle u^2\rangle'_T$ (curve A) were neglected. Thus if it is assumed that curve F does faithfully represent $(\partial\langle u^2\rangle_T/\partial T)_{a_Tc_T}$, and taking the above agreement between theory and experiment as a check on curve C, it then follows that the region between curves B and F represents the constant-volume anharmonic effects. Indeed, if we add the difference between curves B and F to the values of $\langle u^2\rangle'_T$ as determined from the Barron and Munn[12] calculations, we get complete agreement with the measured values of $\langle u^2\rangle'_T$ over the entire thermal range, within the experimental error.

Presuming the foregoing analysis to be correct, it appears that the derivative, $\langle u^2\rangle'_T$, is significantly more sensitive to anharmonic effects than the Debye temperature $\Theta^M(T)$. The volume-expansion effect produced by curve C at 600°K represents 22% of the measured value of $\langle u^2\rangle'_{600}$, whereas the volume expansion causes a reduction in $\Theta^M(600)$ of only 11%. Similarly, the constant-volume anharmonic contribution to $\langle u^2\rangle'_{600}$, as evaluated here, represents about 14% of the measured effect, whereas similar influences on $\Theta^M(600)$ are presumed to be only about 3%.

D. Comparison of Debye Temperatures

It is commonly recognized today that one should not expect quantitative agreement between Debye temperatures relating to different averages over the frequency spectrum. In the light of this fact, it is sometimes informative to compare Debye temperatures as determined by different experimental measurements; such a comparison is made in Fig. 4.

The specific-heat Debye temperatures $\Theta^C(T)$ (curve C) were measured by Martin[19] ($3\leq T\leq 30$°K) and calculated from the thermodynamic data of Eichenauer and Schulze[20] by Barron and Munn[10] ($T>30$°K). The dip seen at 150°K is believed to be spurious by the previous authors; no similar anomaly is seen in the $\Theta^M(T)$-T curve.

As pointed out by Herbstein,[1] in the high-temperature region, the weighting factors involved in the average over the frequency spectrum leading to $\Theta^M(T)$ will weight the low-frequency modes more heavily than the similar average leading to $\Theta^C(T)$. In recognition of this, the fact that $\Theta^C(T)>\Theta^M(T)$ ($T>100$°K) appears to be consistent with the frequency-distribution function calculated from the tensor force model of Young and Koppel,[21] as well as with the calculations of Raubenheimer and Gilat,[22] i.e., the large low-frequency peak in the frequency spectrum probably represents a dominant influence on $\Theta^M(T)$, whereas the two higher-frequency peaks in $g(\nu)$ should influence the specific heats more strongly and thus tend to give a higher value of $\Theta^C(T)$.

The elastic constant Debye temperature $\Theta^E(T)$ is

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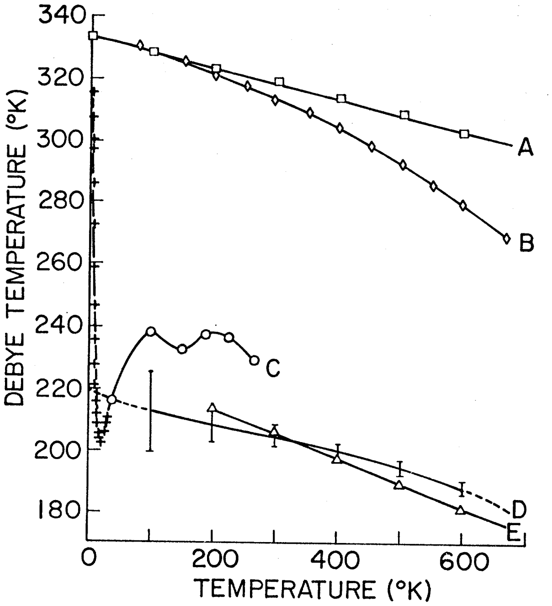

FIG. 4. Thermal variation of the Debye temperature as determined by several methods. Curve A: elastic constant Debye temperature $\Theta^E(T)$ calculated from volume-expansion effects; curve B: elastic constant Debye temperature $\Theta^E(T)$ calculated from elastic constant data; curve C: specific heat Debye temperature $\Theta^C(T)$ [+ measured by Martin (Ref. 19); ○: reported by Barron and Munn (Ref. 10)]; curve D: Debye-Waller Debye temperature $\Theta^M(T)$; curve E: Debye temperature evaluated from the mean square displacement slopes, $\Theta^{M\prime}(T)$.

related to the average lattice wave velocity.[23–25] The problem involved in calculating $\Theta^E(T)$ from the measured elastic stiffnesses $c_{ij}(T)$ is that of performing the average over all the wave velocities. Several methods of evaluating this average without recourse to high speed computers have been proposed in the literature.[24,26–29] The averaging techniques for noncubic systems are complicated by anisotropic effects; methods applicable to hexagonal systems have been developed by Post,[27] Anderson,[28] and Bystrova and Fedorov.[29] An excellent check on the accuracy of the calculation of $\Theta^E(T)$ is the agreement between $\Theta^E(0)$ and $\Theta^C(0)$; theoretically these Debye temperatures should agree at absolute zero.[30] The values of $\Theta^E(T)$ shown in Fig. 4 (curve B) are computed from the elastic constant data of Alers and Neighbours[31] using Anderson's[28] expressions. These results agree with the value of $\Theta^E(4.2)$ of 331.2°K determined from the Bystrova and Fedorov[29] averaging process, as well as with the extrapolated value of $\Theta^C(0)$.

Post attempts to account for the complications of anisotropy by performing the averaging process within the Christoffel equations themselves. However, the results obtained using the same elastic constant data in the Post expressions show serious disagreement with other calculated values of $\Theta^E(T)$; the computed value of $\Theta^E(4.2)$ is 247°K and the extrapolated value of $\Theta^E(0)$ is 247°K. This is in poor agreement with $\Theta^C(\mathbf{0})$ (see curve C). In his tables of the physical properties of the elements, Gschneidner[32] reports that Masing[33] evaluated $\Theta^E(298)$ to be 313°K, which is in excellent agreement with curve B, however Gschneidner chose to use Post's value of 231°K in the tables, because it compared more favorably with $\Theta^C(298)$.

Since the ultrasonic measurements of the elastic constants are related to the very long lattice waves, the calculated values of $\Theta^E(T)$, reflect the behavior of the frequency spectrum for the very low-frequency modes. That $\Theta^E(T)$ falls with increasing temperature confirms the general supposition that the low-frequency slope of the frequency spectrum tends to increase with increasing temperature.

Curve A in Fig. 4 represents the expected decrease in $\Theta^E(T)$ due to lattice expansion effects as calculated from the following expression:

$$\Theta^E(a_T,c_T)=\Theta^E(a_0,c_0)\times[(a_0/a_T)^{2\gamma_a(-3)}(c_0/c_T)^{\gamma_c(-3)}], \quad (15)$$

where the Grüneisen parameters related to the inverse third moment are given by Barron and Munn.[10] It is assumed that the difference between curves A and B can be attributed to constant-volume anharmonic effects. This represents about 8% of $\Theta^M(600)$ and tends to suggest that anharmonic influences are present for the very low frequency modes, as well as for the higher frequencies seen by $\Theta^M(T)$, if one can think of anharmonic effects in $\Theta^M(T)$ as being represented by shifts in the frequency spectrum.

V. CONCLUSIONS

The components of the mean square atomic displacements have been measured for atomic thermal vibrations in the two principal directions in zinc. These measured values of $\langle u_z^2\rangle_T$ and $\langle u_x^2\rangle_T$ have been compared with the calculated values reported by Barron and Munn.[12] At low temperatures ($T<100$°K) the agreement between theory and experiment is very good; the agreement between the measured and calculated values of $\langle u_z^2\rangle_T$ is also quite good over the whole thermal range

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($4.85 \leq T \leq 600$°K). The components of the mean squaer displacements corresponding to vibrations in the basal plane appear to show a discrepancy with the calculated values. This difference tends to increase with increasing temperature, amounting to about 25% of the measured value at 600°K. It is possible that this disagreement between theory and experiment may be due to constant-volume anharmonic effects.

The Debye temperature associated with the mean square displacements, $\Theta^M(T)$, has been evaluated. The extrapolated value of $\Theta^M(0)$ is 219.6°K, which is in excellent agreement with the Barron and Munn[12] computed value. The value of $\Theta^M(T)$ tends to drop with increasing temperature to a value of 187°K at 600°K. This decrease can be explained in terms of volume expansion effects over a broad thermal range ($100 < T < 400$°K). Above 400°K an additional effect appears to be present which is presumed to be attributable to constant-volume anharmonic contributions.

The temperature derivatives of the mean square displacement, $\langle u^2\rangle'_T$, have been evaluated from the data. These measured values of $\langle u^2\rangle'_T$ have been compared with theory and appear to be more sensitive to anharmonic effects than Debye temperature itself. An analysis of the constituent parts of $\langle u^2\rangle'_T$ has led to an evaluation of the constant-volume anharmonic contributions to $\langle u^2\rangle'_T$. When these anharmonic effects are included in the values of $\langle u^2\rangle'_T$ determined from the Barron and Munn[12] calculations, reasonable agreement is realized with the measured results over the thermal range involved.

Finally, the x-ray Debye temperature has been compared with the Debye temperatures as determined from specific heats $\Theta^C(T)$ and from the elastic constant data $\Theta^E(T)$. The fact that $\Theta^C(T) > \Theta^M(T) (T > 100$°K) appears to be consistent with calculated frequency spectra for zinc.[21,22] Over the whole thermal range $\Theta^E(T) > \Theta^M(T)$, this is consistent with similar results for most materials.[11,32]

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