

Exponential Temperature Dependence of Young's Modulus for Several Oxides

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Young's modulus was measured over the temperature range 77°–850°K by an accurate resonance technique. Data are presented for single crystals of aluminum oxide with various orientations of the crystallographic axes and for polycrystalline aluminum oxide, thorium oxide, and magnesium oxide. The results show that the range of validity of a T^4 temperature dependence predicted by theory must be quite small. The temperature dependence is very well described over the whole temperature range by $T \exp(-T_0/T)$, where T_0 is an empirical parameter.

I. INTRODUCTION

THE temperature dependence of the elastic constants of nonmetallic crystals should be given by the theory of lattice dynamics in terms of a set of parameters specifying the interatomic forces including anharmonic terms. Unfortunately, the summations involved are so complicated that apparently no general solution has ever been given. Born and Huang¹ do show that at sufficiently low temperatures the elastic constants should vary as T^4 , but make no estimate of the range of validity of this approximation. The third law of thermodynamics requires that the derivative of any elastic constant with respect to temperature must approach zero as the temperature approaches absolute zero, and the T^4 law satisfies this condition. No general prediction has been made for the form of the temperature dependence at high temperatures, but for many crystalline solids an approximately linear dependence is observed. In particular, a linear temperature dependence has been observed² for Young's modulus of several refractory oxides including aluminum oxide, magnesium oxide, and thorium oxide above room temperature, with the exception that a departure from this linearity is observed in polycrystalline oxides at sufficiently high temperatures (about 1250°K for aluminum oxide, 1500°K for magnesium oxide, and 1400°K for thorium oxide) which may be caused by grain boundary slip. Some justification for a linear behavior at high temperatures can be obtained from a Grüneisen-type approximate equation for the volume compressibility given by Born and Huang.³ This equation gives a T^4 dependence at low temperatures and at high temperatures it gives a term linear in T multiplied by a power series in $(\Theta/T)^2$ which reduces to a constant for $\Theta/T \ll 1$. These refractory oxides have high values of the Debye characteristic temperature ($\Theta = 1045^\circ\text{K}$ for aluminum oxide, $\Theta = 946^\circ\text{K}$ for magnesium oxide, and $\Theta = 782^\circ\text{K}$ for thorium oxide), and offer a good opportunity to examine

the change from linear behavior at high temperature to zero slope at absolute zero. The temperature dependence of the elastic properties should not be complicated by free electron effects because these oxides are all insulators.

The present work has two main objectives: first, an examination of the transition from linear behavior at high temperatures to zero slope at low temperatures with the particular goal of determining whether there is an appreciable temperature range in which the T^4 law holds; and second, the discovery of a function which accurately describes the temperature dependence over the whole range of measurement. The following qualitative argument suggests a form for trial. The linear dependence at high temperatures is probably characteristic of such a high degree of excitation of the vibrational modes that the classical specific heat of k (Boltzmann's constant) per mode is valid. As the temperature is lowered, the slope of the Young's modulus-temperature curve must decrease from a constant value, say B , at high temperatures, to zero at absolute zero. This suggests an equation of the form

$$E = E_0 - BTf(T), \quad (1)$$

where $f(T)$ is a function which approaches one at high temperatures, and zero at absolute zero. We expect $f(T)$ to be related to the degree of excitation of the vibrational modes and try the simplest such function, a single Boltzmann factor $\exp(-T_0/T)$. The suggested equation is then

$$E = E_0 - BT \exp(-T_0/T). \quad (2)$$

This equation gives $E = E_0$ at absolute zero and approaches this value with zero slope as required by the third law of thermodynamics. At high temperatures, $\exp(-T_0/T)$ approaches one, and the equation gives a linear dependence.

II. SPECIMENS

The single-crystal specimens of aluminum oxide (Al_2O_3 in the corundum structure) were grown by the Verneuil flame-fusion process and supplied by the Linde Company. Spectroscopic analysis indicated that the major impurity was Si in the range of 0.01–0.1%. The crystals were ground into rods 6-in. long and with

¹ M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1956).

² J. B. Wachtman, Jr., and D. G. Lam, Jr., *J. Am. Ceram. Soc.* **42**, 254 (1959).

³ The Grüneisen-type approximation for the volume compressibility is given on p. 51 of reference 1. The conclusion that the exact theory gives a T^4 dependence of elastic constants at low temperature is given on p. 327.

TABLE I. Properties of oxide specimens.

Material	Specimen No.	θ (deg)	ϕ (deg)	E_0 (10^{12} dyne/cm ²)	E_0/E_{25}	B (10^8 dyne/cm ²)	B/E_{25} ($10^{-4}/^\circ\text{K}$)	T_0 ($^\circ\text{K}$)	σ (10^{12} dyne/cm ²)
Single crystals									
Al ₂ O ₃	12	39.1	+24.5	3.6905±0.0004	1.0215±0.0001	6.43±0.02	1.781±0.004	267±2	0.0006
Al ₂ O ₃	14	1.0	...	4.6378±0.0001	1.0082±0.0001	4.41±0.01	0.958±0.002	373±2	0.0002
Al ₂ O ₃	15	18.8	+10.5	4.2911±0.0001	1.0131±0.0001	5.45±0.01	1.287±0.002	319±2	0.0003
Al ₂ O ₃	17	40.7	-28.3	4.1424±0.0004	1.0160±0.0001	6.14±0.02	1.505±0.008	305±3	0.0006
Al ₂ O ₃	18	59.5	-29.1	4.3714±0.0002	1.0129±0.0001	5.57±0.01	1.291±0.003	325±2	0.0004
Al ₂ O ₃	19	64.8	-0.8	3.9816±0.0002	1.0170±0.0001	6.03±0.01	1.540±0.003	295±2	0.0005
Al ₂ O ₃	25	89.0	-3.6	4.3015±0.0002	1.0117±0.0001	5.14±0.01	1.209±0.002	335±2	0.0002
Polycrystalline specimens									
Al ₂ O ₃	72.3	3.4629±0.0004	1.0149±0.0001	4.83±0.02	1.395±0.005	309±3	0.0005
Al ₂ O ₃	96.1	4.0532±0.0005	1.0147±0.0001	5.60±0.03	1.402±0.007	312±5	0.0009
MgO	118.0	1.0272±0.0002	...	1.902±0.006	215±4	...
ThO ₂	87.1	2.0416±0.0003	1.0223±0.0002	2.73±0.01	1.367±0.004	181±3	0.0004

diameters in the range 0.1–0.15 in. The orientations are given in Table I in terms of the angles θ and ϕ . The former is the angle between the cylinder axis and the crystallographic c axis; the latter is the angle between the crystallographic $+a$ axis and the projection of the cylinder axis on the crystallographic c plane. These angles and their measurement have been previously discussed.⁴

The polycrystalline aluminum oxide specimen labeled 72.3 was made from powdered aluminum oxide by the McDanel Refractory Porcelain Company by conventional cold pressing and sintering. The density was 3.721 g/cm³ (the single-crystal density is 3.986 g/cm³ at 25°C), and spectrographic analysis indicated the presence of Fe, Ga, Si, and V in the range 0.01–0.1%. Polycrystalline aluminum oxide specimen 96.1 was made by the General Electric Company using a new sintering process⁵ which produced a density of 3.974 g/cm³. Spectroscopic analysis indicated Mg in the range 0.1–1%.

The polycrystalline magnesium oxide specimen (MgO in the rock salt structure) was made by hydrostatic cold pressing followed by sintering. The density was 3.50 g/cm³, and the single-crystal density determined by x-ray lattice-parameter measurement⁶ is 3.581 g/cm³ at 25°C. Spectroscopic analysis indicated the presence of Al, As, Fe, and Si in the range 0.01–0.1%.

The polycrystalline thorium oxide specimen (ThO₂ in the fluorite structure) was made by the Norton Company by conventional cold pressing and sintering. The density was 9.07 g/cm³, and the single crystal density determined from x-ray lattice parameter measurement⁶ is 9.991 g/cm³. Spectroscopic analysis indicated the presence of Al, Mg, and Si in the range 0.01–0.1%. All

polycrystalline specimens were in the form of rectangular bars.

III. EXPERIMENTAL PROCEDURE

The value of Young's modulus for each single-crystal rod at 25°C was determined by measuring the density, dimensions, and longitudinal resonance frequency. The measurements and subsequent calculations of Young's modulus have been described.⁴ For the polycrystalline bars, Young's modulus at 25°C was calculated from the flexural resonance frequency using Pickett's⁷ theory and the interpolation equation of Spinner, Reichard, and Tefft.⁸ Letting E , l , and f represent Young's modulus, the length of the specimen, and the flexural resonance frequency at any temperature, it follows for a specimen with isotropic thermal expansion that

$$E = E_{25}(f/f_{25})^2(l_{25}/l), \quad (3)$$

where the subscripts indicate values at 25°C. This equation follows at once from writing the Young's modulus equation at two temperatures and combining the two equations. For the aluminum oxide single crystals, the thermal expansion is nearly isotropic, but the small anisotropy was taken into account as described in Appendix I.

The procedure for determining the flexural resonance frequency at elevated temperatures by suspending the specimen on two fine glass threads near the nodes has been described.² Low-temperature measurements were made by attaching small magnets to the ends of the specimen and suspending it in a cryostat on threads at the nodes. Small coils in the vicinity of these magnets served as transducers between the specimen and the external electronic equipment. The flexural resonance frequencies were in the range 1–2 kc/sec and were measured with a crystal-controlled counter having an accuracy of 0.1 cps on a 10-sec count, and 0.01 cps on a

⁴ J. B. Wachtman, W. E. Tefft, D. G. Lam, and R. P. Stinchfield, J. Research, Natl. Bur. Standards **64A**, 213 (1960).

⁵ J. E. Burke and S. P. Mitoff, Bull. Am. Ceram. Soc. **38**, 722 (1959).

⁶ H. E. Swanson and E. Tatge, National Bureau of Standards Circular No. 539 (U. S. Government Printing Office, Washington, D. C., 1953), Vol. I.

⁷ G. Pickett, Proc. Am. Soc. Testing Materials **45**, 846 (1945).

⁸ S. Spinner, T. W. Reichard, and W. E. Tefft, J. Research Natl. Bur. Standards **64A**, 147 (1960).

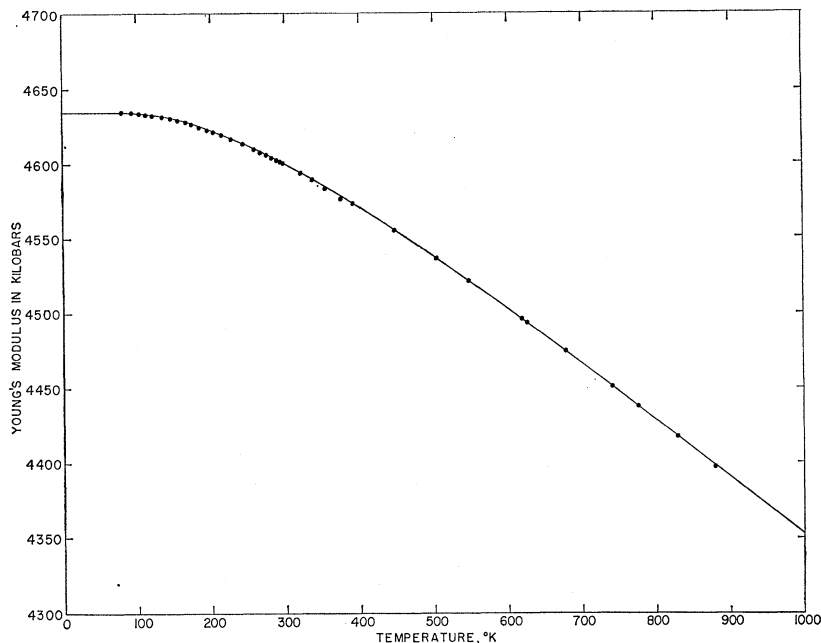


FIG. 1. Young's modulus of single-crystal Al_2O_3 specimen 14 as a function of temperature. The curve is a plot of Eq. (2) using the parameters of Table I.

100-sec count. In the worst case, 0.1 cps error in 1 kc/sec, an error of one part in 5000 in Young's modulus would result from error in frequency measurement. The average error to be expected from this source would be about eight parts in 10^5 on the 10-sec count and two parts in 10^5 on the 100-sec count (the latter error being partly due to oscillator instability). The value of E_{25} is not this accurate, but the ratio E/E_{25} should be, provided the ratio (l_{25}/l) is known this accurately. For single-crystal aluminum oxide and for polycrystalline aluminum oxide and thorium oxide, the thermal expansion was measured for us by T. G. Scuderi and G. W. Cleek, of the National Bureau of Standards, using an interferometer.⁹ The thermal expansion of polycrystalline magnesium oxide was determined by R. K. Kirby, of the National Bureau of Standards, using a fused silica dilatometer. In all cases, the results are believed to be so accurate that less than one part in 10 000 error is caused in E/E_{25} . For aluminum oxide, an integrated form of the Grüneisen equation for thermal expansion was fitted to the data with a standard deviation of 7×10^{-6} in l_{25}/l , so that the random error in these thermal-expansion results is well below one part in 10 000. The largest error in E/E_{25} probably results from error in temperature measurement, and the very small scatter in the data are probably attributable to this cause. This can be shown by plotting the E vs T data on a highly expanded scale. At low temperatures, where dE/dT is very small, the scatter in the data is just the amount to be expected from the error in frequency measurement indicated above, while at high temperatures, where dE/dT is large, the scatter is proportional to dE/dT and almost

⁹ J. B. Wachtman, T. G. Scuderi, and G. W. Cleek, J. Am. Ceram. Soc. (to be published).

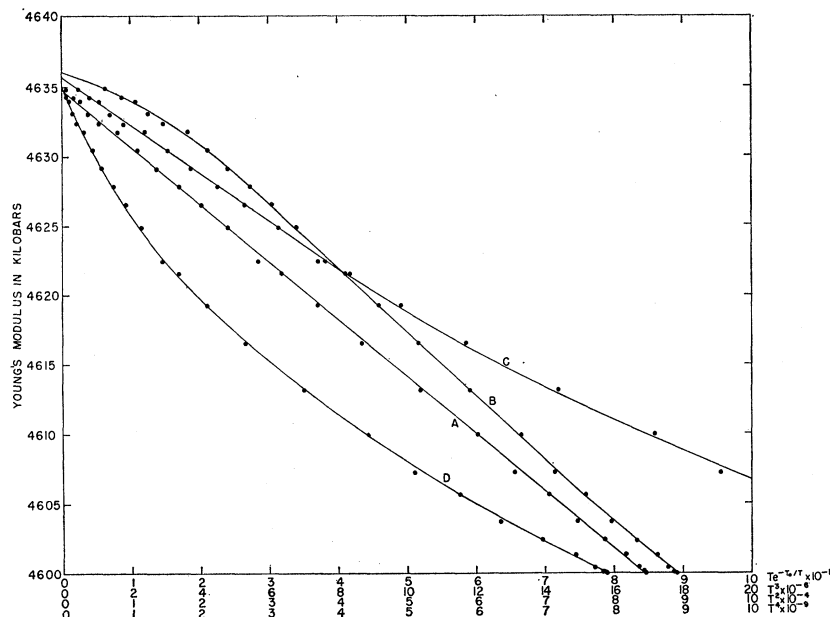
independent of whether the 10-sec or 100-sec count is used.

IV. RESULTS

Typical experimental results are shown in the form of points on the plot of Young's modulus as a function of temperature in Fig. 1. The curve shown in this figure is a plot of Eq. (2) using least-squares best estimates of E_0 , B , and T_0 . The procedure for obtaining the least-squares best estimates is given in Appendix II. Evidently, Eq. (2) fits the data very well. A quantitative measure of the fit is given in Table I, where the column headed σ gives the standard deviation of the measured values from the plotted curves. These values indicate a deviation of only 1 or 2 parts in 10 000 from the plotted curves which is no larger than the estimated experimental error.

A test of the validity of various power laws is given in Fig. 2, where the measured values are successively plotted against T^2 , T^3 , T^4 , and $T \exp(-T_0/T)$. If Young's modulus is correctly represented by one of these functions, the corresponding plot should be a straight line. The function $T \exp(-T_0/T)$ gives a continuously changing curvature when plotted against T , and we expect any power of T to approximate it over some short temperature interval. Thus at sufficiently high temperature, T approximates $T \exp(-T_0/T)$. At somewhat lower temperature, T^2 will approximate $T \exp(-T_0/T)$ over a short temperature range. Successively higher powers will give approximations over successively shorter temperature intervals centered about successively lower temperatures. The plots in Fig. 2 show this behavior. Thus, it is hard to say whether the initial linear portion of the T^4 plot is the theoretical T^4 behavior predicted by Born and Huang or just an ap-

FIG. 2. Young's modulus of single-crystal Al_2O_3 specimen 14 as a function of various functions of temperature. The abscissas for curves A through D are given below the figure in order from top to bottom.



proximation to the function $T \exp(-T/T_0)$ over a limited temperature interval. A more definite check would require Young's modulus measurements with accuracy greater than one part in 10 000 and measurements at lower temperatures. In any case, significant curvature in the T^4 plot is evident at $T=150^\circ\text{K}$ and, below this temperature, Young's modulus is so nearly constant that any true T^4 term which exists must have a small coefficient. If very accurate measurements were made down to 4°K , it might be preferable to use a crystal with a lower value of the Debye temperature. Choice of a high Debye temperature has the advantage of giving a larger range in which to look for the T^4 behavior, but from analogy to the specific heat curves, we might expect that the coefficient of the T^4 term would be smaller for high Debye temperature.

The effect of porosity on the parameters of Eq. (1) is shown by the data on the two polycrystalline aluminum oxide specimens. Specimen 96.1 has a porosity of 0.0030 (defined as 1 minus the ratio of the specimen density to the single-crystal density) and specimen 72.3 has a porosity of 0.0665. The specimen with the higher porosity has lower values of E_0 and B as would be expected. However, the relative change in E with temperature is the same for both specimens. That is, E_0/E_{25} is the same for both specimens within experimental error as are B/E_{25} and T_0 .

The 0.01–0.02% fit obtained for the present data with Eq. (2) is considerably better than the 0.2% fit obtained by Overton and Gaffney¹⁰ for c_{44} of copper using an exponential of the form $F e^{-B\alpha T}$, where F is a function of the volume, α is the linear expansion coefficient, and B is an empirical constant.

V. DISCUSSION

Although no theoretical justification for Eq. (2) is known, the success with which it describes the temperature dependence of Young's modulus suggests that a physical interpretation of the parameters in this equation should be sought. The parameter E_0 should be just the Young's modulus value at absolute zero, and its variation with orientation should be predicted by the theory of elasticity in terms of the single-crystal elastic constants. The qualitative argument given in the Introduction suggests that T_0 should show a correlation with the Debye temperature. The parameter B/E_{25} should be related to Grüneisen's constant γ . This is reasonable on qualitative grounds; the change of Young's modulus with temperature is an anharmonic property and Grüneisen's constant is a simple average measure of anharmonicity. The relation is not likely to be one of simple proportionality, however, because the Grüneisen-type approximation for the volume compressibility derived by Born and Huang¹ contains a linear and a quadratic term in γ . For single crystals, there is the complication that both B/E_{25} and T_0 depend on orientation. This is reasonable; we cannot expect to describe the anharmonic properties for vibrations in different directions by an orientation-independent parameter B , nor can we expect to specify the degree of thermal excitation for different directions of vibration at a given temperature by an orientation-independent parameter T_0 . Orientation-independent parameters γ and Θ suffice for the volume thermal expansion and the specific heat, respectively, because these properties involve averages over all directions.

In the absence of any knowledge of the exact relationship of B/E_{25} and T_0 to other physical properties, we can only compare these values for polycrystalline materials

¹⁰ W. C. Overton, Jr., and John Gaffney, Phys. Rev. **98**, 969 (1955).

TABLE II. Debye characteristic temperature and Grüneisen constant.

Material	Θ (°K)	γ
Al ₂ O ₃	1045±6	1.18 single crystal
		1.34 polycrystalline
MgO	946±4	1.45 single crystal
		1.52 polycrystalline
ThO ₂	782±7	1.78 polycrystalline

with the values of γ and Θ , respectively. Use of polycrystalline materials eliminates the problem of orientation dependence. The Grüneisen constant can be calculated from

$$\gamma = V\alpha K/C_v, \quad (4)$$

where α is the volume thermal expansion, C_v is the specific heat at constant volume, and V is the molar volume. Values of the bulk modulus K for the polycrystalline oxides were taken from Lang¹¹ and corrected to zero porosity using Mackenzie's¹² equation. The bulk modulus for single-crystal aluminum oxide⁴ and single-crystal magnesium oxide¹³ were used to calculate values of γ also. The specific heat of aluminum oxide is given by Furukawa *et al.*,¹⁴ that of magnesium oxide by Barron *et al.*¹⁵ and that of thorium oxide by Osborne and Westrum.¹⁶ The Debye temperature for magnesium oxide is given directly by Barron *et al.*¹⁵ The values of the Debye temperature for aluminum oxide and thorium oxide were calculated from the above-mentioned specific heat data using

$$\Theta^3 = \frac{12\pi^4 Nk}{5(C_v/T^3)}, \quad (5)$$

where N is the number of atoms per mole and k is Boltzmann's constant. The value of C_v/T^3 at 0°K was determined by fitting a straight line to a plot of c_p/T^3 as a function of T^2 and extrapolating to absolute zero.¹⁷

The calculated values of Θ and γ are given in Table II. A qualitative correlation of T_0 for the polycrystalline oxides with Θ exists. Increasing Θ from ThO₂ through

Al₂O₃ is accompanied by increasing T_0 but Θ/T_0 is not constant. No correlation of B/E_{25} with γ is apparent. Evidently, the physical interpretation of the parameters B/E_{25} and T_0 presents a challenging theoretical problem.

APPENDIX I

The anisotropic thermal expansion may be approximately taken into account as follows: Pickett⁷ gives as the relation between Young's modulus E and the flexural resonance frequency f of specimens having rectangular or circular cross sections

$$E = Al^3 f^2 / I, \quad (6)$$

where l = length of specimen, I = moment of inertia of the cross-sectional area about an axis perpendicular to the plane of vibration, and A is proportional to the mass but nearly independent of the shape of the specimen.

If we assume that the same form of equations holds for specimens of the shape used in this study (approximately elliptical, with major and minor axes nearly equal), then we may write

$$E = Al^3 f^2 / ba^3, \quad (7)$$

where a is the cross-sectional dimension in the plane of vibration and b is the cross-sectional dimension perpendicular to this plane. Then

$$\frac{E(T)}{E_{25}} = \frac{f^2(T)}{f_{25}^2} \frac{l^3(T)}{l_{25}^3} \frac{b_{25}}{b(T)} \frac{a_{25}^3}{a^3(T)} \cong \frac{f^2(T)}{f_{25}^2} \left(1 + \frac{3\Delta l}{l_{25}} - \frac{\Delta b}{b_{25}} - \frac{3\Delta a}{a_{25}} \right), \quad (8)$$

where $\Delta l/l_{25}$, $\Delta b/l_{25}$, and $\Delta a/a_{25}$ are the changes in the length and cross-sectional dimensions with temperature. For the symmetry of sapphire, the fractional change in length in any direction is given by

$$\epsilon = \epsilon_{33} \cos^2 n + \epsilon_{11} \sin^2 n, \quad (9)$$

where ϵ_{33} and ϵ_{11} refer to the fractional changes in length along the c axis and perpendicular to the c axis, respectively, and n is the angle between the c axis and the direction of measurement.

In order to specify n for the a and b directions, we must define a new angle ψ , the angle between the plane of vibration and the plane containing the c axis and rod axis. We then obtain

$$\cos n_l = \cos \theta, \quad (10)$$

$$\cos n_a = \sin \theta \cos \psi, \quad (11)$$

$$\cos n_b = \sin \theta \sin \psi, \quad (12)$$

¹¹ S. M. Lang, National Bureau of Standards Monograph 6, 1960 (unpublished).

¹² J. K. Mackenzie, Proc. Roy. Soc. (London) **B63**, 2 (1950).

¹³ H. B. Huntington, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1958), Vol. 7, pp. 213-351.

¹⁴ G. T. Furukawa, T. B. Douglas, R. E. McCoskey, and D. C. Ginnings, J. Research, Natl. Bur. Standards **57**, 67 (1956).

¹⁵ T. H. K. Barron, W. T. Berg, and J. A. Morrison, Proc. Roy. Soc. (London) **250A**, 70 (1959).

¹⁶ D. W. Osborne and Edgar F. Westrum, Jr., J. Chem. Phys. **21**, 1884 (1953).

¹⁷ T. H. K. Barron and J. A. Morrison, Phys. Rev. **115**, 1439 (1959).

where n_l , n_a and n_b are the values of n in the l , a , and b directions, respectively. This gives

$$\frac{\Delta l}{l} = \epsilon_{33} \cos^2\theta + \epsilon_{11} \sin^2\theta, \tag{13}$$

$$\frac{\Delta a}{a} = \epsilon_{33} \sin^2\theta \cos^2\psi + \epsilon_{11}(1 - \sin^2\theta \cos^2\psi), \tag{14}$$

$$\frac{\Delta b}{b} = \epsilon_{33} \sin^2\theta \sin^2\psi + \epsilon_{11}(1 - \sin^2\theta \sin^2\psi), \tag{15}$$

$$1 + \frac{3\Delta l}{l_{25}} - \frac{\Delta b}{b_{25}} - \frac{3\Delta a}{a_{25}} = 1 - \epsilon_{11} + (\epsilon_{33} - \epsilon_{11}) \times [3 \cos^2\theta - \sin^2\theta(1 + 2 \cos^2\psi)]. \tag{16}$$

APPENDIX II

The least-squares best estimates for the parameters in Eq. (2) can be determined by successive approximations using a Taylor series expansion about an initial estimate for T_0 . This initial estimate, denoted T_{01} , is obtained by using three measured values of E and T to write Eq. (1) three times for simultaneous solution. Using

$$e^{-T_0/T} = e^{-(T_{01} + \Delta T_0)/T} \cong (1 - \Delta T_0/T)e^{-T_{01}/T}, \tag{17}$$

we have

$$E \cong E_0 - BT e^{-T_{01}/T} + B(\Delta T_0)e^{-T_{01}/T}. \tag{18}$$

The least-squares best estimates for the unknowns E_0 , B , and $B\Delta T_0$ can be found by standard least-squares techniques. The value $T_{02} = T_{01} + \Delta T_0$ is used as a new initial estimate and the process repeated until the change ΔT_0 is within the standard deviation. In practice, two repetitions were sufficient.