THE ABSOLUTE THERMAL EXPANSION OF COPPER AND ALUMINUM
BETWEEN 5 K AND 330 K

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Ph. D. Thesis Submitted to Iowa State University

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The absolute thermal expansion of copper and aluminum
between 5 K and 330 K

by

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TABLE OF CONTENTS

	Page
CHAPTER I. INTRODUCTION	1
Basic Theory	5
Lattice contribution	6
Electronic states' contribution	15
Total expansion coefficient	17
Copper and Aluminum Data Survey	18
Experimental Methods	22
CHAPTER II. APPARATUS	32
Capacitance Dilatometer	35
Characterization of Samples	42
Capacitance Measurement	45
Thermometry	51
CHAPTER III. RESULTS	58
Experimental Procedure	58
Analysis of Data	61b
Copper	64
Aluminum	73
Sources of Error	81
CHAPTER IV. DISCUSSION AND CONCLUSIONS	90
Conclusions	97
REFERENCES	99
ACKNOWLEDGEMENTS	103
APPENDIX A. EXPERIMENTAL DATA	104
APPENDIX B. FINITE TEMPERATURE INTERVAL CORRECTION	115

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The absolute thermal expansion of copper and aluminum
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The linear thermal expansion coefficients α of copper and aluminum have been measured in an absolute sense between 5 K and 330 K. Only the sample, supported by glass spacers in a copper cell, changed temperature during a thermal expansion measurement. Sample length changes were detected as changes in the capacitances of the two three-terminal, parallel-plate capacitors between the sample and cell ends. A three-terminal, ratio-transformer, ac capacitance bridge was used with a phase-sensitive detector to measure the nominally 10 pF capacitances to a precision of 10^{-7} pF; changes of $0.02 \text{ \AA}$ in the 10-cm sample length could be detected. The $\alpha(T)$ data were fit with fifth order polynomials in four overlapping temperature ranges; the sets of fit coefficients, tabulations of smoothed values, and deviation plots of the data from the smoothed fits are given in the text. The absolute accuracy of the smoothed results ranges from $\pm 0.1\%$ above 50 K to $\pm 0.5\%$ near 20 K and $\pm 1\%$ at 10 K, reflecting the scatter in the data. The results of other measurements on copper and aluminum during the past 20 years also are compared to the present results

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via deviation plots. The 1954 results of Rubin, Altman, and Johnston for copper (1) and their 1955 results for aluminum (2) agree with the present results above 60 K within 0.5% and 1%, respectively. However, the 1970 measurements on copper by Hahn (NBS) (3) show systematic deviations of 2% or more below 100 K. Under 35 K the present results agree well within the combined experimental error with the 1972 copper results of McLean, Swenson, and Case (4) and of White and Collins (5), and with the 1973 aluminum results of Collins, White, and Swenson (6). On the basis of the present results, copper and aluminum now may readily serve as thermal expansion reference standards below room temperature.

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CHAPTER 1. INTRODUCTION

Thermal expansion is the isobaric change in the dimensions of a substance due to a change in temperature. The volume thermal expansion coefficient β is defined by

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P. \quad (1-1)$$

A linear thermal expansion coefficient α can be defined as

$$\alpha_i = \frac{1}{L_i} \left(\frac{\partial L_i}{\partial T} \right)_P \quad (1-2)$$

for each principal axis ($i = 1, 2, 3$) of an anisotropic crystal. If the solid is isotropic, such as a cubic metal, only one linear expansion coefficient exists, and $\alpha = \beta/3$, where β is given by Equation (1-1).

Two other related differential thermodynamic quantities are the heat capacity and the bulk modulus. These three derivatives, when measured over a range of temperature and pressure, plus a reference point $P_0(V_0, T_0)$, completely characterize a solid.

In many areas of technology, a knowledge of the temperature dependence of the dimensions of the components of an assembly is necessary. Most thermal expansion measurements of technological materials are differential in nature; i.e., they are referenced to some standard material. Hahn of the National Bureau of Standards (NBS), in response to a technological need for a thermal expansion reference material, published in 1970, the thermal expansion coefficient of a specific lot

of copper (NBS Standard Reference Material 736) over the temperature range 20 K to 800 K (1). However, White (2) has pointed out that inconsistencies exist between Hahn's results and a number of previous measurements, with differences near 1% or more at many temperatures. These inconsistencies are disturbing, since the relevant properties of a reference material should be known to an accuracy an order of magnitude greater than is required for routine applications. For example, copper has been given the role of a standard reference material for heat capacity measurements, and in 1968 Furukawa et al. (3) at NBS critically analyzed existing copper heat capacity data and gave selected mean values for C_p from 0 to 300 K. These have an estimated uncertainty limit which decreases from $\pm 0.5\%$ below 50 K to $\pm 0.2\%$ above 100 K. Comparable accuracy would be desired for copper as a thermal expansion reference standard.

Aluminum also has potential as a thermal expansion reference material. Like copper, it has a face-centered cubic structure, is readily obtained in large, high purity samples, and is easily machined into suitable form. Much less work has been done on the thermal expansion of aluminum than for copper.

The present work describes high precision measurements of the thermal expansion coefficients of copper and aluminum over a wide range of temperatures. Useful results extend from 5 K to 325 K for copper and 10 K to 330 K for aluminum. Only the sample changed dimensions during a thermal expansion measurement, so the measurements are absolute in that they are not referenced to any other material. Except at the

lowest temperatures, the accuracy is $\pm 0.1\%$. Copper and aluminum were chosen because of their potential as thermal expansion reference materials and because considerable experimental and theoretical work has been done on these over a wide range of temperatures. The existence of two reference standards, rather than one, whose thermal expansion coefficients have been measured in an absolute sense in one apparatus, is very useful to check for systematic errors in another apparatus, by measuring aluminum with respect to or along with copper in the other apparatus and comparing the results to the present results. The present highly accurate results for the thermal expansion coefficients of copper and aluminum should become a valuable reference for technological work.

Precision measurements of the thermal expansion coefficient also are valuable theoretically in the construction of microscopic models of solids (4). The quality of agreement between the predictions of a theoretical model and the corresponding experimental measurements is the strongest test a model must face.

The major problems in thermal expansion measurement become apparent when the magnitude of α is considered over a wide range of temperatures. The linear thermal expansion coefficient may be obtained either by differentiating an experimental length versus temperature $L(T)$ curve, or by approximating Equation (1-2) by

$$\bar{\alpha} = \frac{1}{L} \left(\frac{\Delta L}{\Delta T} \right)_P, \quad (1-3)$$

where ΔL is the finite change in length due to the finite temperature change ΔT . Consider copper at 300 K with a thermal expansion coefficient α_{Cu} of about $1.7 \times 10^{-5} \text{ K}^{-1}$ which varies slowly with temperature. A 1 cm long rod would expand by $\Delta L \approx 17,000 \text{ \AA}$ ($10^8 \text{ \AA} = 1 \text{ cm}$) for $\Delta T = 10 \text{ K}$. A simple measurement technique based on optical interferometry is suggested when this ΔL is compared to the wavelength of light ($\sim 5000 \text{ \AA}$), and resolution to a few percent of an interference fringe is ample for a 1% thermal expansion measurement.

A 30 K, α_{Cu} has decreased to 10^{-6} K^{-1} and varies significantly with temperature. Smaller temperature intervals must be used, and the same 1 cm rod now has a ΔL of only 300 $\text{\AA}$ for a ΔT of 3 K. A 1% measurement now requires a 3 $\text{\AA}$ resolution (about 0.1% of a fringe) which is beyond the capability of simple interferometry techniques. Measurements at 5 K are even more demanding with $\alpha_{\text{Cu}} \approx 5 \times 10^{-9} \text{ K}^{-1}$, and varying rapidly ($\sim T^3$), so that very small temperature intervals ($\Delta T \approx 0.5 \text{ K}$) must be used. To be theoretically useful, the thermal expansion coefficient must be determined to one or two percent, so ΔL must be resolved to $\sim 0.01 \text{ \AA}$ even with a 10 cm long sample. Special high-sensitivity techniques are needed for measurements at these low temperatures. The present results were obtained with one such high-sensitivity technique, a capacitance dilatometer, with a sensitivity of about 0.02 $\text{\AA}$ independent of temperature.

The following sections of this chapter present a discussion of thermal expansion theory, a brief summary of previous thermal expansion

measurements on copper and aluminum, and a description of several experimental methods, particularly capacitance dilatometer methods.

Basic Theory

The thermodynamic relations between the macroscopic properties of solids were formulated long before reliable methods existed for relating bulk properties to the microscopic properties of the atoms which form the solid. All of the bulk thermodynamic properties of a solid are contained in the Helmholtz free energy $F(V,T) = U - TS$, where U is the internal energy, T the absolute temperature, and S the entropy.

(Additional independent variables would have to be introduced in the case of a magnetic solid, for example.) The various derivatives of F give: the equation of state

$$P(V,T) = - \left(\frac{\partial F}{\partial V} \right)_T, \quad (1-4)$$

the entropy

$$S(V,T) = - \left(\frac{\partial F}{\partial T} \right)_V, \quad (1-5)$$

the heat capacity at constant volume

$$C_V(V,T) = \left(\frac{\partial U}{\partial T} \right)_V = - T \left(\frac{\partial^2 F}{\partial T^2} \right)_V, \quad (1-6)$$

the isothermal bulk modulus

$$B_T(V,T) = - V \left(\frac{\partial P}{\partial V} \right)_T = V \left(\frac{\partial^2 F}{\partial V^2} \right)_T, \quad (1-7)$$

and the volume thermal expansion coefficient

$$\beta(V,T) = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = \frac{1}{B_T} \left(\frac{\partial P}{\partial T} \right)_V = - \frac{1}{B_T} \left(\frac{\partial^2 F}{\partial T \partial V} \right)_{T,V}. \quad (1-8)$$

The detailed form of $F(V,T)$ depends on the choice of a theoretical model of the solid. At thermal equilibrium, the simplest approximation assumes that the various contributions to the free energy (lattice vibrations, "free" electrons, magnetic interactions, etc.), and hence to the derivatives, are additive. If they are not additive, but interact in some cooperative fashion, it is difficult to make anything but specific calculations. This work is concerned with high purity nonmagnetic metals and thus it is assumed that thermal expansion contributions arise only from the lattice vibrations and the conduction electrons.

Lattice contribution

In 1926, Grüneisen (4) proposed a simple model for the lattice dynamics of a solid from which he concluded that the thermal expansion coefficient should be proportional to the heat capacity as

$$\beta = \gamma C_V / B_T V, \quad (1-9)$$

where γ , a dimensionless number of the order of unity, is the Grüneisen parameter. The product $B_T V$ varies only slowly with temperature, and experimentally the relationship (1-9) holds surprisingly well, particularly at "high" temperatures. Deviations from the Grüneisen theory are observed experimentally. Barron (5,6) and Blackman (7) first made

theoretical calculations using more realistic models of the lattice vibration spectrum than Grüneisen, and showed that deviations could be expected with the greatest departure from Grüneisen's theory occurring at temperatures of the order $\theta_0/5$, where θ_0 is the characteristic Debye temperature at $T=0$. Other subsequent calculations are in qualitative agreement with Barron and Blackman.

The lattice expansion results from anharmonic effects in the crystal potential energy. It has been shown that an idealized crystal with nearest neighbor harmonic forces would exhibit no thermal expansion; such a solid would be mechanically unstable, however, and no such crystals exist (6). Consider a lattice of N atoms and the $3N$ displacement components x_i from equilibrium. Expanding the lattice potential energy ϕ in a Taylor's series about equilibrium (volume V_0), one obtains in general

$$\phi = \phi(V_0) + \sum_{i=1}^{3N} \left(\frac{\partial \phi}{\partial x_i} \right)_{V_0} x_i + \frac{1}{2} \sum_{i,j=1}^{3N} \left(\frac{\partial^2 \phi}{\partial x_j \partial x_i} \right)_{V_0} x_i x_j + \dots, \quad (1-10)$$

where $\phi(V_0)$ is the static lattice potential energy at equilibrium. Since the expansion is about equilibrium, $(\partial \phi / \partial x_i)_{V_0} = 0$ for all i . If the summation is truncated after the second-derivative term, the harmonic approximation results; the second derivatives $(\partial^2 \phi / \partial x_j \partial x_i)_{V_0}$ are the coupling force constants of the lattice, and the solution of the coupled oscillator problem gives the $3N$ normal modes ω_i of the crystal. The harmonic approximation is sufficient to calculate the

heat capacity; but to calculate the thermal expansion, the quasi-harmonic approximation is used in which the higher order terms in Equation (1-10) are merged into the lower order terms such that

$$\phi = \phi(V) + \frac{1}{2} \sum_j \left(\frac{\partial^2 \phi}{\partial x_j^2} \right)_V x_j^2, \quad (1-11)$$

where $\phi(V)$ is the static lattice potential energy at volume $V(T)$, and the coupling force constants are volume dependent, since V depends on the average displacements $\bar{x}_i(T)$. Solving for the normal modes now gives $\omega_i = \omega_i(V)$ with explicit volume dependence.

If these $3N$ normal modes $\omega_i(V)$ are assumed to be independent, their contributions to the Helmholtz free energy are additive and one obtains a sum over Einstein oscillator terms, (8)

$$\begin{aligned} F(V, T) &= U_0(V) + \sum_{i=1}^{3N} F_i(V, T) \\ &= U_0(V) + \sum_i \frac{1}{2} \hbar \omega_i(V) + \sum_i \ln(1 - e^{-\hbar \omega_i(V)/k_B T}). \end{aligned} \quad (1-12)$$

The three terms represent the configuration, zero point, and thermal energies. Equation (1-8) can then be used to obtain the thermal expansion coefficient as

$$\beta = \sum_i \beta_i = \frac{1}{B_T V} \sum_i \gamma_i C_{u_i}, \quad (1-13)$$

where

$$\gamma_i = - \left(\frac{\partial \ln \omega_i(V)}{\partial \ln V} \right)_T \quad (1-14)$$

is the Grüneisen parameter and

$$C_i = - T \left(\frac{\partial^2 F_i}{\partial T^2} \right)_V = k_B \left(\frac{\hbar \omega_i}{k_B T} \right)^2 \exp\left(\frac{\hbar \omega_i}{k_B T}\right) \left[\exp\left(\frac{\hbar \omega_i}{k_B T}\right) - 1 \right]^{-2} \quad (1-15)$$

is the Einstein heat capacity for the i^{th} mode. Grüneisen's relation for the bulk solid, $\gamma = \beta B_T V / C_V$, now follows if γ is defined as

$$\gamma = \sum_i \gamma_i C_i / \sum_i C_i \quad (i = 1, \dots, 3N). \quad (1-16)$$

Gamma can have an explicit temperature dependence (usually small) since the γ_i 's may differ for different lattice vibration modes. The product $B_T V$ is constant (to a first approximation); hence the thermal expansion coefficient, Equation (1-13), is expected to be almost proportional to the heat capacity. This is a statement of Grüneisen's original relation, and is experimentally found to be valid for many solids over wide temperature ranges with γ approximately constant and between 1 and 3 in magnitude. At sufficiently high temperatures ($T \gg \theta$, the characteristic Debye temperature), all modes are excited and $C_i = k_B$, and γ approaches a constant limiting value

$$\gamma \rightarrow \gamma_\infty = (1/3N) \sum_i \gamma_i. \quad (1-17)$$

At low temperatures ($T \ll \theta$), the most direct approach is to assume that the lattice free energy can be expressed as $F(V, T) = T f(T/\theta)$, where the volume dependence of F is due entirely to the volume dependence of a characteristic temperature $\theta(V)$. It follows immediately from Equation (1-6) that the heat capacity is $C_V(V, T) = g(T/\theta)$, and after differentiating in Equation (1-8), Grüneisen's relation ($\gamma = \beta B_T V / C_V$) is obtained with

$$\gamma = - \left(\frac{\partial \ln \theta}{\partial \ln V} \right)_T. \quad (1-18)$$

At sufficiently low temperature ($T \ll \theta_0$), the Debye model is valid and the heat capacity is given by

$$C_V = (12/5) \pi^4 N k_B (T/\theta_0)^3 = b T^3. \quad (1-19)$$

The Grüneisen's relation implies that the lattice contribution to the thermal expansion coefficient at low temperatures is

$$\beta = B T^3, \quad (1-20)$$

where B is a constant.

As $T \rightarrow 0$, γ approaches a limiting value

$$\gamma_0 = \Sigma_i \gamma_i v_i^{-3} / \Sigma_i v_i^{-3}, \quad (1-21)$$

where v_i is the velocity of the i^{th} mode ($i = 1, \dots, 3N$) (9).

In this limit the lattice may be treated as an elastic continuum, and

if each mode is assigned a characteristic temperature $\theta_i = (\hbar/k_B) q_m v_i$, where q_m is the maximum allowed wave-vector for the continuum, then Equation (1-21) may be rewritten as

$$\gamma_o = \frac{1}{3} (\partial \ln \Sigma_i \theta_i^{-3} / \partial \ln V)_T = - (\partial \ln \theta_o / \partial \ln V)_T, \quad (1-22)$$

where

$$\theta_o^{-3} = (1/3N) \Sigma_i \theta_i^{-3}; \quad (1-23)$$

θ_o is the familiar Debye temperature calculated from the velocity of elastic waves at $T = 0$.

For temperatures above the Debye T^3 region, the calculation of the Grüneisen parameter γ^{elas} from elastic constant measurements is more complex, yet valuable since these measurements then can be related to thermal expansion and heat capacity measurements by comparing γ^{elas} with γ^{th} calculated from the thermal measurements. The mode gammas of Equation (1-14) are rewritten in terms of the mode polarization p and wave-vector $\vec{q}$ as

$$\gamma(p, \vec{q}) = - (\partial \ln \omega(p, \vec{q}) / \partial \ln V)_T, \quad (1-24)$$

and similarly the mode heat capacities C_i of Equation (1-15) become $C(p, \vec{q})$. The summation over i becomes an integration over $\vec{q}$ and a summation over p , and Equation (1-16) becomes

$$\gamma^{\text{elas}} = \frac{\int d\Omega q^2 dq \Sigma_p \gamma(p, \vec{q}) C(p, \vec{q})}{\int d\Omega q^2 dq \Sigma_p C(p, \vec{q})}. \quad (1-25)$$

In general, the sum on p must precede the integral over Ω to avoid any ambiguities in the definition of polarizations. Because of crystal symmetry, the angular integration need cover only a fraction (typically 1/16 or less) of 4π steradians. Furthermore, the assumption is made that the excitation of optical modes can be neglected, so that p takes only the values 1, 2, 3 for the acoustic modes.

To perform the calculations in Equation (1-25) it is necessary to choose a dispersion relation $\omega(p, \vec{q})$. The continuum model is introduced with these assumptions (10):

(i) The acoustic modes of the Debye model ($\omega = vq$) have a constant velocity of sound

$$\frac{dv}{d\vec{q}} = 0; \quad (1-26)$$

(ii) The maximum value of q along any direction equals the Debye radius

$$q_D = (6\pi^2/V_0)^{1/3} \quad (1-27)$$

[The volume of the Debye sphere equals that of the first Brillouin zone, and it is $(2\pi)^3$ times the inverse of V_0 , the volume of the primitive unit cell.];

(iii) The acoustic modes are either nondispersive (Debye model), or obey the sinusoidal dispersion relation

$$\frac{\omega}{\omega_{\max}} = \sin\left(\frac{\pi}{2} \frac{q}{q_D}\right) \quad (1-28)$$

of the Born-von Karman model (10);

(iv) The generalized Grüneisen parameters of Equation (1-24) are independent of wave vector magnitude (but not direction) models and are given by their long wavelength ($q \rightarrow 0$) limits.

The choice of a dispersion relation does not affect the generalized gammas of assumption (iv), but does affect their weight in the specialized weighted average of Equation (1-25). For example, at intermediate temperatures ($T \sim \theta/20$) the Born-von Karman model gives greater weight to the low-lying modes than does the Debye model (11). Sheard (12) and Collins (13) investigated several cubic materials in the nondispersive (Debye) model. Brugger and Fritz (11) extended their approach to include sinusoidal dispersion (Born-von Karman model) and arbitrary crystal symmetry. Inclusion of dispersion improved the agreement between $\gamma^{\text{elas}}(T)$ as calculated from elastic data, Equation (1-25), and the experimental $\gamma^{\text{th}}(T)$ obtained from thermal expansion and heat capacity measurements, Equation (1-9).

A further refinement to the above calculation uses the actual dispersion relation $\omega(p, \vec{q})$ as determined from neutron scattering experiments, and calculations (14, 15) for copper and silver are in close agreement with experimental results. The magnitude of the decrease (see Figure 19) from γ_m to γ_0 [Equations (1-17) and (1-21)] is not changed significantly, but the temperature range in which the decrease occurs is brought (lowered) closer to the experimental γ^{th} behavior. The dispersion relations are available for copper from Nilsson and Rolandson (16) and for aluminum from Stedman, Almqvist, and Nilsson (17).

The mode gammas, Equation (1-24), are not readily obtained from neutron spectrometry. Using Equation (1-7), the mode gammas may be expressed as a pressure derivative

$$\gamma(p, \vec{q}) = B_T \left(\frac{\partial \ln(p, \vec{q})}{\partial P} \right)_T, \quad (1-29)$$

where $\gamma \sim 2$ and $B_T \sim 1400 \text{ kbar}$ ($14 \times 10^{10} \text{ N/m}^2$) for copper. To obtain γ to about 1%, a pressure of about 70 kbar would have to be applied to change ω by 10%, assuming that the frequencies are measured to 0.1% (typical). Pressures of this magnitude are well beyond the practical working range of neutron spectrometers.

The mode gammas can be determined from elastic constant (velocity of sound) measurements. Consider a Debye solid for which

$$\omega(p, \vec{q}) = q s_p(\theta, \phi), \quad (1-30)$$

where s_p is the velocity of sound and the direction of $\vec{q}$ is now specified by the angles (θ, ϕ) . The effective elastic constant for this vibration mode is

$$c_p(\theta, \phi) = \rho s_p^2(\theta, \phi), \quad (1-31)$$

where ρ is the density of the solid. For a continuum, $\rho \sim V^{-1}$ and $q \sim V^{-1/3}$, and hence Equation (1-24) becomes

$$\gamma(p, \vec{q}) \rightarrow \gamma_p(\theta, \phi) = -\frac{1}{6} - \frac{1}{2} \left(\frac{\partial \ln c_p(\theta, \phi)}{\partial \ln V} \right)_T. \quad (1-32)$$

Experimentally, the pressure dependence of the elastic constants is measured instead of the volume dependence, so the relation

$$\gamma_p(\theta, \emptyset) = -\frac{1}{6} + \frac{1}{2} B_T \left(\frac{\partial \ln c_p(\theta, \emptyset)}{\partial P} \right)_T \quad (1-33)$$

is used in place of Equation (1-32). Measurements of the pressure derivatives of the elastic constants give only the mode gammas for the nondispersive phonons when Equation (1-33) is used, since it was derived assuming no dispersion, Equation (1-30). At high temperatures, the continuum model approximation that the dispersive mode gammas are equal to the nondispersive ones is usually difficult to justify. At temperatures much below the Debye temperature, the nondispersive modes become dominant and the pressure derivatives of the elastic constants provide a direct measurement for the Grüneisen mode parameters (12). Pressures of a few kbars produce a change of about 1% in the ultrasonic transit time (which can usually be measured to better than one part in 10^5), and hence are sufficient for determining the pressure derivatives (18). Elastic constant pressure derivatives for copper and aluminum are given by Daniels and Smith (19) and Ho and Ruoff (18), respectively.

Electronic states' contribution

The conduction electrons also contribute to the bulk thermodynamic properties of a metal. To first order, the contributions to the free energy of the conduction electrons and the lattice vibrations are additive and hence $C_V = C_V^{el} + C_V^{lat}$ and $\beta = \beta^{el} + \beta^{lat}$, where the

superscripts el and lat refer to the electronic and lattice contributions, respectively. A Grüneisen parameter γ^{el} may be defined for the electronic contribution in the same manner as γ^{lat} for the lattice in Equation (1-9):

$$\gamma^{el} = \beta^{el} B_T V / C_V^{el}. \quad (1-34)$$

The thermal expansion coefficient, Equation (1-8), may be rewritten in terms of the entropy, S from Equation (1-5), as

$$\beta = \frac{1}{B_T} \left(\frac{\partial S}{\partial V} \right)_T. \quad (1-35)$$

For conduction electrons, an excellent approximation for the entropy of a volume V of most metals below the melting point is given by

$$S^{el} = (\pi^2/3) k_B^2 T V N(\epsilon_F), \quad (1-36)$$

where $N(\epsilon_F)$ is the density of electronic states per unit volume at the Fermi level, ϵ_F (9, 20). Thus the conduction electrons give rise to an expansion contribution

$$\begin{aligned} \beta^{el} &= (\pi^2/3 B_T) k_B^2 T N(\epsilon_F) \left[1 + \left(\frac{\partial \ln N(\epsilon_F)}{\partial \ln V} \right)_T \right] \\ &= \gamma^{el} C_V^{el} / B_T V, \end{aligned} \quad (1-37)$$

where $C_V^{el} = T(\partial S^{el}/\partial T)_V$ has been used to give the electronic heat capacity at constant volume. The electronic Grüneisen parameter is thus obtained as

$$\gamma^{el} = 1 + \left(\frac{\partial \ln N(\epsilon_F)}{\partial \ln V} \right)_T . \quad (1-38)$$

To a first approximation (spherical Fermi surface), $N(\epsilon_F) \sim V^{-1/3}$, and hence $\gamma^{el} = 2/3$ for free-electron like metals. Little theoretical work has been done to predict values of γ^{el} for real metals (9, 21; 22). If γ^{el} is constant and $B_T V$ varies negligibly with temperature, then, as for the lattice, $\beta^{el}(T)$ should have the same temperature dependence as C_V^{el} . For "low" temperatures ($T \ll \epsilon_F/k_B \approx 6 \times 10^4$ K), the electronic specific heat is proportional to T , (23) and therefore

$$\beta^{el} = AT , \quad (1-39)$$

where A is a constant. For a given metallic solid, γ^{el} is thus determined experimentally from the ratio of the T coefficients of the temperature dependent representation of the thermal expansion and heat capacity data.

Total expansion coefficient

The total low temperature thermal expansion coefficient for a non-magnetic metal will be obtained by combining the electronic term from Equation (1-39) and the lattice term from Equation (1-20). The form of the resulting equation

$$\beta = AT + BT^3 \quad (1-40)$$

should be valid for $T \lesssim 0.02 \theta_0$ where the Debye model provides a suitable approximation of the solid. At temperatures up to about $\theta_0/10$,

where dispersion (non-Debye behavior) is becoming significant, the thermal expansion should behave like the heat capacity with higher order terms involving an expansion in odd powers of the temperature (24). Above $\theta_0/10$, dispersion dominates the lattice contribution, which in turn dominates the electronic contribution, and no unique power series expansion in the temperature is possible.

It is necessary to go to very low temperatures where β^{el} is significantly greater than β^{lat} so that it may be measured with reasonable accuracy. It was not possible to extend the present measurements to sufficiently low temperatures to estimate the electronic contribution to the thermal expansion coefficient.

Copper and Aluminum Data Survey

Published thermal expansion measurements generally may be separated into two categories: low temperature, extending up to 35 or 40 K, and "high" temperature, extending down to 20 K from (typically) room temperature. In the following listings, the year, the method, and the temperature range are mentioned. Some common methods are briefly described in the next section of this chapter, but for complete information, the cited paper should be examined. The results of the cited measurements are compared graphically to the present results in Chapter III on Figures 13 and 18.

Low temperature results for copper have been published by Carr, McCammon, and White (25) (1964, capacitance dilatometer, 5-30 K), by

Carr and Swenson (26) (1964, variable transformer, 3-15 K), by Shapiro, Taylor, and Graham (27) (1964, optical lever, 4-55 K), by Kos and Lamarche (28) (1969, capacitance dilatometer, 4-15 K), by Periera, Barnes, and Graham (29) (1970, optical lever, 3-10 K), by McLean, Swenson, and Case (30) (1972, variable transformer, 2-35 K), and by White and Collins (31) (1972, capacitance dilatometer, 2-35 K). As White and Collins have pointed out (31), the earlier (25-30) low temperature measurements disagree quantitatively (often by as much as 10%) and even qualitatively with each other for reasons which are not altogether clear. Recently, Periera and Graham (32) conducted a study of specimen-dependent effects and suggest that an impurity-dislocation interaction may be the cause of anomalous expansion. The most recent thermal expansion coefficient results of White and Collins using a differential capacitance dilatometer (with a sensitivity of roughly 10^{-10} in $\Delta L/L$) and the results of McLean et al. using a linear differential transformer technique (with a sensitivity of about 2×10^{-11}) agree to within $\pm 5\%$ at low temperatures and to within 2% above 20 K. They conclude (30) that the averaged thermal expansion coefficient results probably are accurate in an absolute sense to $\pm 2\%$ at all temperatures within the range of investigation (2 K to 35 K). The present work included this low temperature range as a check on this conclusion, and the present results lie between the results of McLean et al. and of White and Collins.

Published thermal expansion measurements for copper at higher temperatures include Rubin, Altman, and Johnston (33) (1954, interferometer, 25-295 K), Bijl and Pullan (34) (1955, capacitance dilatometer,

40-275 K), Simmons and Balluffi (35) (1957, x-ray, 30-80 K; and 1963, x-ray, above 300 K), Leksina and Novikova (36) (1963, quartz pushrod strain gauge dilatometer, 90-1320 K), Rhodes, Moeller, Hopkins, and Marx (37) (1963, quartz pushrod interferometer, 18-573 K), Fraser and Hollis Hallett (38) (1965, interferometer, 20-90 K), Lifanov and Sherstyukov (39) (1968, quartz pushrod strain gauge dilatometer, 90-570 K), Bunton and Weintroub (40) (1968, optical lever/grid, 10-200 K), Cooper and Yates (41) (1970, interferometer, 10-240 K), Hahn (1) (1970, interferometer, 20-80 K), Awad and Guban (42) (1971, capacitance dilatometer, 10-80 K), Pojur and Yates (43) (1973, interferometer, 300-800 K), and also White and Collins (31) (1972, capacitance dilatometer, 55-85 K). At temperatures from 120 K to 220 K, there is close agreement (within 0.5%) between the data of Rubin et al., Hahn, Leksina and Novikova, and Lifanov and Sherstyukov. Outside of this temperature range, the results of Hahn (NBS) systematically disagree with the other three (Rubin, L & N, L & S) by over 0.5% near 270 K and by nearly 2% near 90 K. Hahn's data (1) also show considerable scatter at low temperatures, rising from 2% near 100 K to 50% at 20 K. The present work agrees well with the 1954 results of Rubin et al. above 60 K and connects smoothly, with minimal scatter, to the low temperature ($T < 35$ K) results of White and Collins (31) and McLean et al. (30) as mentioned in the preceding paragraph (see also the figures in Chapter III).

Although aluminum has not received as much attention as copper with respect to thermal expansion measurements, again there is a natural division into low temperature (below 35 K) and high temperature (20 K

and above) published results. The measurements cited below are compared to the present results graphically in Chapter III. The low temperature measurements include White (22) (1961, capacitance dilatometer, 3-15 K), Andres (44) (1961, optical grid, 3-9 K), Carr and Swenson (26) (1964, variable transformer, 3-20 K), and Collins, White, and Swenson (45) (1973, capacitance dilatometer and variable transformer, 2-35 K). The results of Collins et al. were obtained from independent measurements with capacitance and variable transformer dilatometers (increased sensitivity over References 31 and 30) and agree to better than 1% above 12 K and within 3.5% below 12 K. Other measurements of the thermal expansion of aluminum from higher temperatures down to about 20 K include those of Altman, Rubin, and Johnston (46) (1955, interferometer, 30-300 K), of Bijl and Pullan (34) (1955, capacitance dilatometer, 40-270 K), of Gibbons (47) (1958, interferometer, 20-300 K), of Huzan, Abbiss, and Jones (48) (1961, optical lever, 15-100 K), of Rhodes, Moeller, Hopkins, and Marx (37) (1963, quartz pushrod interferometer, 18-573 K), of Fraser and Hollis Hallett (38) (1965, interferometer, 25-80 K), and of Awad and Guban (42) (1971, capacitance dilatometer, 10-75 K). As with copper, there is considerable disagreement among the measurements below 60 K, but the present results agree well with the 1955 results of Altman et al. above 55 K and the low temperature results of Collins et al. between 10 and 35 K. (Refer to the graphical comparisons in the figures of Chapter III.)

Experimental Methods

It is convenient to classify methods of thermal expansion measurement into two main types: (i) methods having high sensitivity, which are particularly appropriate to determine the very small dimensional changes encountered when small coefficients of thermal expansion are being measured; and (ii) methods suitable for continuous operation over extended ranges of temperature, in which the overall changes in length may be relatively large (several tenths of one percent in $\Delta L/L$). It is unusual to find these two major advantages in any one method; each method generally involves a compromise between high length change sensitivity and wide useful temperature range.

The high sensitivity techniques usually are limited in their useful temperature range. Three common types are the optical grid (44), the optical lever (27, 29, 32, 48), and the variable transformer (26, 30, 45) dilatometers. A fourth sensitive technique using a capacitance dilatometer can be designed to operate over an extended range of temperatures and will be discussed later.

Optical techniques can be used with fractional angstrom sensitivity by measuring the change in light transmission through two grids, one stationary and the other attached to the sample (44, 49). The stationary grid has alternate transparent and opaque bands of equal width while the movable grid is identical except for the central opaque band which is double width. If the two grids are matched for maximum transmission over half their area, the remaining half will allow zero transmission.

As the sample expands and the attached grid moves, the transmission through one half will increase while the transmission through the other half will decrease. The transmitted light from each half is sensed by photocells and the signals are combined in a "bridge" circuit using a differential amplifier. The sensitivity can be increased by closer spacing of the opaque grid bands, but the maximum allowable total length change of the sample is reduced. Over the distances involved, the output is linear with grid position and provisions are made to calibrate the apparatus mechanically.

A companion to the above technique uses a doubly twisted "Ayrton" strip which is attached to the sample to convert linear motion into rotation of the strip (27, 29). The angular position of a small mirror attached to the center of the strip is measured using an optical lever. The apparatus is calibrated at room temperature by fitting the high temperature measurements to those obtained from other sources. Room temperature measurements with the optical grid have been used to detect length changes of 10^{-4} Å (50). However, at low temperature, measurements with both methods have demonstrated 0.1 to 1 Å sensitivity (27, 29, 44, 49). A merger of these two optical techniques reflects the image of one grid off a mirror which is tipped by sample expansion. The image is focused on the second grid and transmitted light intensities are measured with photocells (40). Similar sub-angstrom sensitivities are attained. The problem of getting light into the sample region without introducing errors from heating complicates the measurements with these optical techniques.

A technique that has demonstrated the highest sensitivity at low temperatures uses a variable differential transformer (26, 30, 45). The transformer consists of two coils: a primary located in the liquid helium bath and a coaxial, astatic secondary which is attached to the sample and mounted inside a vacuum jacket. A 35 gauss primary field induces approximately equal and opposite voltages in the secondary coil, and since the primary field varies along the axis, this induced voltage is a function of secondary position. Changes in sample length are transmitted mechanically to the secondary coil and the resulting output voltage (or coupling to the primary) is measured using a stable mutual inductance bridge. A tertiary winding on the primary provides a stable mutual inductance reference. The method is absolute in that only the sample changes temperature, and with careful winding of the coils, it enjoys the advantage of a calibration against bridge readings which is linear with sample position over a 2 mm range and is temperature independent. Changes in length as small as $0.01 \text{ \AA}$ can be detected although stability problems normally limit the data precision to $0.02 \text{ \AA}$, a relative precision of 2×10^{-11} for a 10 cm sample. Experimental problems have proven more troublesome for this method than for the capacitance dilatometer methods (discussed below and in later chapters) since there is no magnetic equivalent of the electrostatic guarding which is realized in a three-terminal capacitance bridge, and great care must be taken to insure that temperature-dependent eddy currents, superconducting transitions, etc. do not introduce spurious effects during the measurements. In addition, this is strictly a low temperature

technique since its high sensitivity depends on the low residual resistivity of the many thousand turn copper coils.

The thermal expansion methods which are applicable over a wide range of temperatures usually lack the high sensitivity of the above techniques, and generally are useful only above 20 K. X-ray techniques measure the actual lattice spacing, whereas other common thermal expansion respond to the bulk temperature dependence of an average lattice spacing, including the effects of vacancies and other crystal defects, so results must be compared carefully. The bulk thermal expansion methods which are useful at high(er) temperatures are the interferometer types and the capacitance dilatometers.

Optical interferometry has been a popular tool for thermal expansion measurements (1, 33, 37, 38, 41, 43, 46). The several versions which have been used are similar in operating principle. Often, two quartz optical flats form a Fabry-Perot etalon with the sample, either in the shape of three small rods of equal length or a hollow cylinder, acting as the spacer. Monochromatic light incident perpendicularly on the flat surfaces produces interference fringes. As the sample lengths change, the fringes move and each fringe which passes a fiducial mark represents a sample length change equal to one-half wavelength of the light used. The sensitivity is limited by the ability to measure a fraction of a fringe, typically ± 0.01 fringe, which yields a length resolution of about 50 Å. Recently, Jacobs et al. (51) described a modification useful near room temperature and above which uses a modulated laser. The sideband frequency resonates with the etalon,

and thus changes with sample length. The resolution in $\Delta L/L$ of 10^{-9} (1 Å for a 10 cm sample) is limited by the stability of the laser. Other variations use quartz rods to transmit sample length changes to the interferometer plates (37) or to a strain gauge (36, 39) which are located at room temperature.

These interferometry techniques are absolute in that the sample length changes are measured directly, not relative to another material (except for possible corrections for the small thermal expansion of quartz in the pushrod types). Normally, the sample length is measured as a function of the temperature, and the results are differentiated to obtain the thermal expansion coefficient. With α typically 10^{-5} K^{-1} , a precision of 10^{-8} K^{-1} is needed for 0.1% accuracy and is (somewhat) beyond the reach of the normal interferometry techniques.

Another method for the measurement of thermal expansion over a wide range of temperatures is based on the (reciprocal) relationship between plate separation and capacitance in a parallel plate capacitor. High sensitivity needed at low temperatures also is achieved with proper design. Three different geometries of capacitance dilatometer cells are sketched in Figure 1. A three-terminal capacitor configuration is used for each, in that the capacitors are completely shielded with the effective area of the capacitor plates determined by a grounded guard ring (including the rest of the cell) as the third terminal. An ac ratio-transformer bridge (described in the chapter on apparatus) is used to measure the small capacitance between the plates (1-10 pF) with

Figure 1. Capacitance dilatometer cells with the normal, inverted, and absolute geometries.

high precision (10^{-7} pF) in spite of the presence of large shunting capacitances (2000 pF) to ground. An older version, as used by Bijl and Pullan (34), placed the capacitor in the resonant circuit of an rf oscillator, and sample length changes were reflected in oscillator frequency shifts, allowing 1% thermal expansion measurements after the apparatus was properly calibrated with a reference material.

In the "normal" geometry cell of Figure 1, as pioneered by White (25, 52), the top end of the metal sample (or a copper plate attached to an insulating sample) forms a parallel plate capacitor with a guarded fixed plate in the top of the normally copper cell. The gap between the plates varies with temperature according to the difference between the thermal expansions of the sample and the cell. A modified version with "inverted" geometry (the middle cell in Figure 1) which is used by Swenson and coworkers (53-58) has a central copper post suspended from a plate which rests on the top of the samples (three rods of equal length). The bottom of the post forms a parallel plate capacitor with a guarded fixed plate in the bottom of the surrounding cell. The gap between the plates varies with temperature according to the difference between the thermal expansions of the samples and the copper post. The differential change in gap length, in both the "normal" and "inverted" geometries, is observed as a change in the measured capacitance, hence the label "differential capacitance dilatometer." The copper cell or post acts as a thermal expansion reference.

The capacitance of two parallel plates is related to the separation L_g and the area A of the plates by

$$C = (\epsilon_o A / L_g) . \quad (1-41)$$

The sensitivity to change in separation, which is given by

$$\frac{dC}{dL_g} = - \frac{\epsilon_o A}{L_g^2} , \quad (1-42)$$

decreases rapidly with increasing separation of the plates. If the thermal expansion of the sample is larger than that of the copper cell, the separation of the plates increases and the sensitivity decreases as the "normal" cell is taken to low temperatures where increased sensitivity is needed. The "inverted" cell, with the same sample material, has its minimum sensitivity at higher temperatures where less sensitivity is needed. An additional problem arises with both types of cells when the thermal expansion of the sample is much smaller than that of the copper cell or post. Since most of the measured capacitance change is due to the cell (or post) expansion, the thermal expansion of the copper reference material must be known with high accuracy in order to calculate the sample thermal expansion with an accuracy of a few percent. White has turned this behavior to his advantage by using a sample (silicon) of known low thermal expansion to measure the thermal expansion of his copper cell (31). The required thermal equilibrium between the sample and the cell (or post) in all differential capacitance dilatometers is achieved using exchange gas, but this necessitates an additional isothermal jacket around the cell to contain the gas.

The third capacitance dilatometer design shown in Figure 1 was used in the present experiment and avoids some of the problems of the above-mentioned differential cells. The sample rests on thermally and electrically insulating spacers inside a cell, with parallel plate capacitors at each end. The two capacitors are used to locate the two ends of the sample with respect to the ends of the cell. Since

$$L_{\text{cell}} = L_{\text{sample}} + L_{g1} + L_{g2}, \quad (1-43)$$

if the cell temperature, and hence its length, is held constant while the sample temperature is changed for an expansion measurement, then

$$\Delta L_{\text{sample}} = - (\Delta L_{g1} + \Delta L_{g2}), \quad (1-44)$$

and the sample thermal expansion measurement is absolute, not relative to the cell expansion as in a differential dilatometer. Equations (1-41, 42) are used to obtain $L_{g1,2}$ and $\Delta L_{g1,2}$ from the measured capacitances. Neither the exact temperature nor the thermal expansion coefficient of the cell need be known. No exchange gas is involved. Like the "normal" cell, this "absolute" cell loses some sensitivity at low temperatures with samples which have a much larger thermal expansion than the copper cell, so this "absolute" capacitance dilatometer is ideally suited to sample materials which have a thermal expansion which is comparable to (or smaller than) the copper cell. One additional advantage which this arrangement has over all other absolute dilatometers (including the interferometer types) is that the ends of the sample are located directly, without the introduction of an interface (quartz to

sample, for instance) which could have an expansion of its own. However, precision absolute measurements are much more difficult to make than are differential measurements, so they are done only when a reference material is under study. Additional thermometry is required, and temperature stability is a major experimental consideration. Differential measurements generally are quite adequate when accuracy to about 1% in the sample thermal expansion coefficient is satisfactory.

CHAPTER II. APPARATUS

The cryostat and electrical systems used in the present experiment are described in this chapter. Figures 2 and 3 present the apparatus in general terms; details are given in the following sections.

Figure 2 shows an outline (1/10 scale) of the cryostat in a conventional glass dewar system which can be used with liquid nitrogen and liquid helium refrigerants. When full, the nitrogen and helium dewars hold about 20 and 30 liquid liters, respectively. The liquid nitrogen may be frozen and the liquid helium made superfluid through reduction of their vapor pressures by pumping; vibration due to bubbling of the liquids is thereby eliminated. The main flange (Figure 2) supporting the dewars rests on a platform which is designed for isolation from laboratory mechanical vibration. Added vibration isolation is given by flexible couplings in the pumping lines. The capacitance dilatometer (the "absolute" geometry of Figure 1) is contained in a brass vacuum can which is suspended at the end of the 1-in. diameter stainless steel pumping tube.

The electrical systems consist of a capacitance bridge, temperature sensing and control systems, and heaters. Figure 3 gives a block diagram of the electrical systems; the components are briefly identified here and are discussed in detail in later sections of this chapter. The capacitance bridge is used to measure (alternately) the capacitance of the two parallel plate capacitors of the "absolute" geometry capacitance dilatometer cell (see Figure 1). A dc potentiometric comparison method is

Figure 2. The cryostat and dewar system.

Figure 3. A block diagram of the electrical systems. The points labeled A through E correspond to those in Figures 4 and 5.

used to measure the resistance of germanium (GE) and platinum (PT) resistance thermometers to determine the sample temperature. A constant current supply (CCS) feeding the sample heater is used to manually control the sample temperature. The cell temperature is controlled automatically by an ac temperature controller (ACTC in Figure 3) which uses a carbon resistor or a platinum resistance thermometer as a temperature sensor in an ac bridge arrangement to regulate the power input to the cell heater. The support post, from which the cell is suspended inside the vacuum can, has a heater driven by a constant current supply. The vacuum can also has a heater; its use is described below. Differential thermocouples are used to monitor the temperature differences between the sample, cell, support post, and vacuum can.

Capacitance Dilatometer

Details of the capacitance dilatometer used in the present work are shown in Figure 4. The brass vacuum can is 10.5 in. (26.7 cm) tall and has a diameter of 3.5 in. (8.9 cm). A 100- Ω heater of #36 manganin resistance wire was noninductively wrapped around the can, uniformly distributed over the length of the can, and secured with GE-7031 varnish. When there was no refrigerant in the inner (helium) dewar, this heater was used to control the temperature of the vacuum can. The can temperature is monitored with a thermocouple (see below).

Two types of vacuum seals were made for the capacitance and other electrical leads entering the vacuum can. The miniature coaxial cable (0.020 in. nominal o.d., Uniform Tubes, type UT-20-SS) has a stainless

Figure 4. The vacuum can and capacitance cell. The points marked A through D are the locations of differential thermocouple junctions.

steel outer conductor, so soft solder vacuum seals could be made, simultaneously grounding the outer conductor. The inner conductor of the miniature coax is a silver-plated, copper-clad steel wire with a dc resistance of about $1\ \Omega$ per foot; the dielectric is FEP teflon. Two coaxial cables enter the vacuum can via one feed-thru; a third cable enters through a second feed-thru which is not shown in Figure 4. Vacuum seals for all the other electrical leads, an assortment of #38 copper and #30 manganin wires, were made by potting Stycast epoxy (Emerson and Cuming, type 2850-GT/catalyst 9) around the wires at the ends of two stainless steel tubes (one is not shown in Figure 4). The vacuum can was soldered onto its top with Wood's metal as the last step in the dilatometer assembly.

The thin-wall stainless steel tube support post which extends down from the top of the vacuum can in Figure 4 is a continuation of the pumping tube. A pumping hole is cut into one side of the post. A $100\text{-}\Omega$ heater of #36 manganin resistance wire was wrapped around the middle of the post and secured with Stycast, with a layer of nylon mesh between the wire and the stainless steel post to insure electrical insulation. This heater is used to limit the heat flux from the capacitance cell up the post when the cell is much warmer than the vacuum can.

The capacitance cell hangs from the support post. A manganin resistance wire (#36) heater was wrapped noninductively around the cell in two bands of $100\ \Omega$ each near the top and the bottom of the cell wall and secured with Stycast, again with a layer of nylon mesh under the wire. The post and cell heater arrangement was intended to reduce the possibility of a temperature gradient in the cell wall.

The top and bottom (capacitance) plates of the cell and the cylindrical cell wall all were made from the same electrolytic tough pitch copper. After rough machining, the pieces were vacuum-annealed at 300°C, and then the mating surfaces were finished flat and parallel to 0.0001 in. (0.0003 cm). The cylindrical part of the cell is 4.0200 in. (10.211 cm) long at room temperature, with an outer diameter of 2.50 in. (6.35 cm). The end plates and cell wall are all 0.250 in. (0.635 cm) thick, and were gold-plated to prevent the development of an unstable oxide coating and to enhance the thermal contact at the mating surfaces. Twenty C-shaped copper strips (drawn to scale in Figure 5) around the middle of the cell (Figure 4) serve as electrical tie points. A layer of nylon mesh insulates the strips which are secured with Stycast. A copper clip holding a carbon resistor and a miniature platinum resistance thermometer ("ACTC SENSORS" in Figure 5) is secured with a screw at a gap in the belt of electrical tie points. As described later in the section on thermometry, these are used as temperature sensors for the cell temperature controller (ACTC).

A vertical cross section of the capacitance cell and sample is shown in Figure 5. The guarded cell ("high-side") capacitor plates of the "absolute" cell of Figure 1 are located in the centers of the identical top and bottom cell pieces in Figure 5. These plates are the faces (0.75 in. (1.91 cm) diameter) of tapered plugs which were insulated with two layers of 0.001-in. (0.025-mm) thick mylar film before being pressed into tapered (2°) holes in the cell ends. This was done before the annealing and final machining. The ends of the copper or aluminum sample

Figure 5. A cross section of the capacitance cell and sample. The points marked A, B, D, and E are the locations of differential thermocouple junctions.

form the corresponding ("low-side") capacitor plates. The designed plate separation, a nominal 0.010 in. (0.25 mm), gives a capacitance of 10 pF which is near the maximum capability of the capacitance bridge used (see below). Hereafter, the upper and lower capacitors are referred to as the "sample" capacitor (C_s) and the "reference" capacitor (C_r), respectively.

Electrical access to the guarded cell-end capacitor plates is shown clearly in Figure 5. Stycast was used to pot a male connector pin onto the end of each coaxial cable, both to provide mechanical strength and to form a vacuum seal against leaks through the cable. The mating female connectors are soldered into the ends of the posts extending from the guarded plates. A similar arrangement exists for the capacitance connection to the sample, but here the female connector is soldered into a hole in a screw in the sample. The teflon shield at the top of the cell in Figure 5 protects the insulation ring around the sample capacitor plug from small metal particles (primarily solder) which sporadically fall down from inside the pumping tube, and which in one experiment shorted the insulating ring. The reference capacitor plug is protected on the outside by a copper pipe cap.

The sample, as shown in Figure 5, is a cylinder nominally 0.020 in. (0.51 mm) shorter than the cell and 1.5 in. (3.8 cm) in diameter. A shelf was cut into one side of the sample and holes were drilled clear through to accept the platinum (PT) and germanium (GE) resistance thermometers. A circular ledge, nominally 0.010 in. (0.25 mm) deep around the base of the sample, accommodates the spacers on which the sample rests. A single layer of nylon mesh was wrapped around the sample before a 100 Ω heater

of #36 manganin resistance wire was wound noninductively over the length of the sample and secured with GE-7031 varnish. Wires from the thermometers and one junction of a differential thermocouple also were wrapped one to two turns around the sample, and were secured with GE-7031 varnish. These serve to thermally anchor the thermometers and thermocouple to the sample. The heater and thermometry leads from the sample pass through a 0.75-in. (1.9-cm) diameter hole in the cell wall to the electrical tie points on the cell, and are either manganin wire (#30 or #36) or copper wire (#38) with a series segment of manganin to provide thermal isolation of the sample from the cell. The capacitance connection to the sample also passes through the hole in the cell wall.

A length of #20 copper wire, one end wrapped three to four times around the bottom of the sample and secured with GE-7031, also comes out the cell wall hole and is routed up to the mechanical heat switch which is mounted on the bottom of the vacuum can top. The lower jaw can be raised remotely from the top of the apparatus to close on the copper wire, completing a low thermal conductivity path from the sample to the liquid helium bath. This allows more rapid cooling of the sample, and when desired, allows the sample temperature to be held below that of the cell. Finally, because they are capacitively coupled to the sample (the common capacitor terminal), the heater, thermometer, thermocouple, and heat switch wires all are grounded appropriately so as not to disturb the capacitance readings.

The three spacers on which the sample rests (see Figure 5) are small glass discs which are spaced at 120° intervals around the sample ledge,

and are held in position by a teflon retainer ring (not shown in Figure 5). The ring helps restrict the transverse motion of the sample. The discs are nominally 0.020 in. (0.51 mm) thick for a 0.010 in. (0.25 mm) reference capacitor plate separation with a sample ledge of 0.010 in. (0.25 mm). Glass was chosen for the spacer material because of its very low thermal conductivity at all temperatures. The discs were made in several steps. Two common microscope slides were waxed together with black DeKhotinsky cement to form a sandwich. Six to eight discs were made at one time using a diamond abrasive core bit to cut through one slide. This was the most difficult step, and some of the raw discs were lost since the wax tended to fracture during the drilling. The sandwich was placed in a grinding machine* and the slide with the cut discs then was ground down to the desired thickness. The ground surface was polished partially before the wax was melted to remove the discs. The four to six successful discs which were obtained from each sandwich generally had the same thickness to ± 0.0004 in. (0.01 mm) or less. Three discs with the desired thickness to ± 0.0001 in. (0.003 mm) were selected from two or three such sandwiches.

Characterization of Samples

Material for the copper sample was obtained from the American Smelting and Refining Company (ASARCO) in the form of a long rod. It

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*Kindly made available by Dr. D. L. Biggs of the Earth Science Department. The "thin section grinder" is normally used to prepare thin slices of rock for microscope analysis.

was electron-beam melted in a vacuum (to remove gases and some impurities) into a cylindrical ingot suitable for machining. Sample Cu-3 of McLean et al. (30) also was prepared from the ASARCO rod, so the present results may be compared closely to the Cu-3 measurements below 35 K. The aluminum was received from Cominco Aluminum Incorporated (COMINCO) as a cylindrical ingot already suitable for machining. A semiquantitative mass spectroscopy impurity analysis was performed on material from each sample; the results are given (in atomic ppm) in Table 1. As a rule-of-thumb, the quoted values may be in error by a factor of three, high or low; values quoted as "less than" (<) represent detection limits. Vacuum fusion analysis for hydrogen, nitrogen, and oxygen and combustion analysis for carbon also were performed on the aluminum sample, and these results are included as footnoted entries in Table 1; error limits also are a nominal factor of three. There appear to be no significant impurities. Another measure of bulk impurity content is the residual resistivity ratio ($\rho_{300K}/\rho_{4.2K}$). Measurements were made on annealed slices of the copper and aluminum material. For copper the measured ratio was 1500, and for aluminum the ratio was 2000. These values are typical of high purity material and are consistent with the analysis results in Table 1.

The copper sample was annealed at 300°C for one hour before the ends were finished (light machining and grinding) flat and parallel to 0.0001 in. (0.003 mm). The measured (micrometer) length of 3.999₆ in. (10.159 cm) agrees with the value of 3.999₅ in. calculated from room temperature capacitance measurements and a cell length of 4.020₀ in., which

Table 1. Impurity analysis results for the ASARCO copper and COMINCO aluminum samples. All impurities are given in atomic ppm; those not listed have a concentration of 1 ppm or less. (Spark source mass spectrographic analysis except as noted.)

	ASARCO copper	COMINCO aluminum
H	--	25 ^a
C	20	100, 45 ^b
N	0.5	8, 2 ^a
O	15	50, 25 ^a
Mg	6	<2
Al	<3	--
Si	≤30	<100
S	--	3
Cl	5	10
Ti	4	--
V	2	--
Fe	2	3
Cu	--	0.5
Zn	--	3
Y	2	--
Gd	<2	--
Er	<5	--
Lu	<5	--
Ta	5	--
W	10	<3

^aVacuum fusion analysis.

^bCombustion analysis.

was obtained with an electronic feeler gauge and a precision 4.0000 in. gauge block reference.

The aluminum sample also was annealed (200°C for one hour) before its ends were finished. Due to a measurement error, it was made slightly shorter than the copper sample, and the bottom ledge was cut a bit deeper. The measured (micrometer) length of the aluminum sample is 3.991_0 in. (10.137 cm) and the calculated length is 3.991_2 in. The ledge was cut 0.013 in. (0.33 mm) deep instead of 0.010 in. (0.25 mm). So thicker glass spacers (nominally 0.028 in. or 0.71 mm) were made for the aluminum sample such that the sample and reference capacitor gaps would be comparable in size (about 0.015 in. or 0.38 mm) at low temperature. Since the aluminum sample has a thermal contraction ($\Delta L/L$) between 300 K and 4 K roughly $4/3$ that of the copper cell, the sample capacitor gap is about 0.011 in. (0.28 mm) at room temperature. The shorter aluminum sample, with the larger capacitor gaps, resulted in a length change sensitivity at low temperatures which was smaller by a factor of two when compared with that for the copper sample. This was unfortunate but not disastrous.

Capacitance Measurement

The capacitance of the sample and reference capacitors was measured with a three-terminal capacitance bridge; a simplified bridge schematic is shown in Figure 6. This bridge arrangement, which was suggested by Campbell (59) and developed by Thompson (60), makes possible the measurement of small capacitances, a few picofarads, to a precision of 10^{-7} pF,

AT BALANCE $V_x j\omega C_x = V_s j\omega C_s \Rightarrow C_x = C_s \frac{V_s}{V_x}$

----- SHIELD

Figure 6. The basic three-terminal capacitance bridge. C_x is the unknown capacitance and C_s is the standard capacitor.

in spite of the presence of several thousand pF in cable capacitance. The ratio transformer is used to adjust the voltage input to the standard capacitor (C_s in Figure 6) until the currents in the two arms of the bridge are equal. The balance condition which is given in Figure 6 shows that the unknown capacitance (C_x) is directly proportional to the ratio transformer setting. The plates of the capacitors which are connected to the transformer outputs (high voltage) are the "high sides" and those connected to the detector (low voltage) are the "low sides". The sample ends are the low sides of the sample and reference capacitors, because the thermometers on the sample could be damaged by the voltages available at the transformers. The high side of the reference capacitor was switched to ground when the sample capacitor was being measured, and vice versa.

The detailed circuit of the bridge which was used for the present measurements is shown in Figure 7. The major additions to Figure 6 include the use of two ratio transformers and standard capacitors in a parallel arrangement to obtain higher resolution, and the use of a small circuit to balance the resistive (quadrature) component of the off-balance signal. The connecting cable and other shields are not shown in Figure 7. The 100-pF standard capacitor (General Radio, type 1404-B, S/N-789, 100.0005 pF ± 20 ppm at 25°C) in conjunction with a five dial ratio transformer (Gertsch RatioTran, model RT-60, S/N-714, ± 10 ppm ratio accuracy) which is connected to a 10% tap on the bridge transformer gives a contribution to C_s of Figure 6 of 0 to 11.1110 pF with a resolution of 10^{-4} pF, and was used to balance the unknown capacitance (C_x of Figure 6) to

SHIELDS ARE NOT SHOWN

Figure 7. The detailed capacitance bridge circuit.

10^{-4} pF. The 0.1 pF standard capacitor (General Radio, type 1403-N, S/N-3660, $0.09997 \text{ pF} \pm 0.06\%$ at 25°C) in conjunction with a seven dial ratio transformer (Gertsch AC Ratio Standard, model 1011, S/N-312, ± 2 ppm ratio accuracy) which is connected across the full bridge transformer winding gives a contribution to C_s of Figure 6 of 0 to 0.11111110 pF with a resolution of 10^{-8} pF . This second ratio was set to balance the remaining $<10^{-4} \text{ pF}$ of the unknown capacitance. The two-transformer arrangement allows the balancing of an unknown capacitance (nominally 10 pF) to a resolution of 10^{-8} pF (theoretically). A second five dial ratio transformer (Gertsch, RT-60, S/N-715) was used with the phase shifting components indicated in Figure 7 to balance the resistive component of the off-balance signal.

These ratio transformers are precision inductive voltage dividers the accuracy of which is based on the use of precision tapped autotransformers wound on high permeability toroidal cores. The three-terminal standard capacitors are located in a temperature-controlled box and their effective total capacitance is stable at the 10^{-8} pF level (53, 57). The bridge transformer was locally constructed (53) following the design of McGregor et al. (61). The 1078 Hz oscillator is removed physically from the rest of the bridge to prevent broadcasting by the oscillator transformer to the bridge. The oscillator is capable of delivering a maximum of 300 volts peak-to-peak to the bridge transformer and 140 volts peak-to-peak to the capacitance cell. The null detector is a narrow-band amplifier and lock-in dual phase-sensitive detector of local design and construction (62).

The resolution of the capacitance bridge is limited in practice by the magnitude of the cable capacitance, the sensitivity of the null detector, and the noise in the system. All shields are grounded, so the cable capacitance introduces a finite impedance to ground for all points in the circuit. The capacitance of a cable which connects a transformer to the high side of a capacitor merely shunts the very low output impedance (a few ohms) of the transformer, and, hence, has a negligible effect. The capacitance of a cable which connects the detector to the low side of a capacitor shunts the detector input. The total shunting capacitance across the detector lowers the effective input impedance from about 50 M Ω to typically 100 k Ω . The detector voltage sensitivity which is required to detect a departure from bridge balance of magnitude δC is given by

$$\delta V = V \delta C / C_c, \quad (11-1)$$

where V is the input voltage to the capacitance cell (50 V rms) and C_c is the shunt capacitance on the low side of the system (about 1400 pF), and is primarily cable capacitance. Thus, a voltage sensitivity of about 3.5 nV rms is required to obtain a resolution of 10^{-7} pF. The detector has been modified from Reference (62) to increase the amplifier sensitivity by the substitution of a low noise FET input stage for the nuvistor-tube stage, and of active noise filters (63) for the passive R-C filters on the phase-sensitive detector outputs. This amplifier presently is operating with a shorted-input noise level of 3 nV peak-to-peak (1 nV rms) using a ten-second time constant and a 30 nV full-scale sensitivity. In the presence of noise external to the detector, a resolution of 10^{-7} pF

was achieved with the ten-second time constant, while 5×10^{-8} pF was approached with a time constant of 20 seconds which further reduced background noise. The capacitive (in-phase) and resistive (quadrature) off-balance signals were displayed on separate chart recorders (Moseley, type 7100 B, see Figure 3). The scale for the capacitance off-balance signal was calibrated so that graphical interpolation could be done.

Thermometry

The temperature of the sample was determined by comparing the voltage across the resistance of a calibrated resistance thermometer to that across a standard resistor, carrying the same current, using a standard four-terminal dc potentiometric technique with current reversal to compensate for the effects of thermal emf's (see Figure 3). The germanium (GE) resistance thermometer (Cryo Cal, S/N-748, nominally 340Ω at 4.2 K) was calibrated locally in terms of T_x , a temperature scale based on paramagnetic salt thermometry (64). The platinum (PT) resistance thermometer (Leeds and Northrup, model 8164, S/N-1654277, nominally 25.5Ω at 273 K) was calibrated by the National Bureau of Standards in 1965. The calibration was later referenced to the IPTS-68 scale (65,66).

The standard resistors are Leeds and Northrup wirewound types. A 10- Ω standard resistance (type 4025-B, S/N-1765097, 9.99992Ω at 25°C) was used for the platinum thermometry. The germanium thermometer resistance was compared to a 100- Ω standard resistance (type 4030-B, S/N-1733520, 100.0002Ω at 25°C) at temperatures generally above 5 K, and to a 1000- Ω standard resistance (type 4035-B, S/N-1770735, 999.998Ω at 25°C) at lower temperatures. The standard resistors were initially calibrated by Leeds

and Northrup. The calibrations have since been checked through intercomparison with several similar calibrated standard resistors and are believed to be accurate to 1 part in 10^5 .

The potentiometer is a Guildline type 9176 Nanopot (S/N-26637) used with a 100 mV full-scale range and a least count of 0.1 μ V. An early experience with dial nonlinearity in another potentiometer prompted a linearity check of the Nanopot. Each step of the 10 mV/step dial was compared to the full ten steps of the 1 mV/step dial, and each step of the 1 mV/step dial then was compared to the full ten steps of the 100 μ V/step dial. Although apparently within the manufacturer's specifications, nonlinearity corrections were made to the 1 mV/step dial (-0.04μ V/step) and to the 100 μ V/step dial (-0.014μ V/step). The 10 mV/step dial was assumed to be correct, but its linearity is immaterial since it was not used with the germanium thermometer, and was changed only rarely during measurements with the platinum thermometer.

The thermometer currents and the potentiometer current are obtained from locally-built, temperature-compensated constant current supplies with a stability of about 1 ppm (67). The platinum thermometry was operated at a nominal 2 mA. The germanium thermometry current ranged between 5 and 200 μ A, such that the thermometer voltage generally stayed between 1.5 and 4 mV during a series of thermal expansion measurements. A Keithley model 150A microvolt-ammeter is used on the $\pm 1 \mu$ V full-scale range as a null detector for the potentiometer. The off-balance signal is displayed on one pen of a dual-pen strip chart recorder (see Figure 3) to monitor temperature drifts, if any. (The capacitance off-balance signal is displayed on the other pen.)

The germanium thermometer (and hence T_x) was used for the analysis of data at temperatures up to 35 K, and the platinum thermometer (and hence IPTS-68) was used for the analysis of data at temperatures above 30 K. Swenson (68) recently has published revised differences between T_x (64) and other scales which show an inconsistency with IPTS-68 (65,66) from 20 to 30 K of roughly 10 mK. This was checked and confirmed at 30 K during the present experiment. The distinction between the two scales is not made in the tabulation of smoothed results, since, as Holste et al. (24) have shown in their analysis of copper heat capacity results, a precise definition of the temperature scale is important only at the lowest temperatures. The temperature intervals which were used in the thermal expansion measurements in the overlap region (30 to 35 K) always were made using a single thermometer to eliminate temperature differences which could be caused by different thermometer calibrations.

Sufficient sensitivity is available to just barely resolve a 0.1 mK temperature change with the platinum thermometer (a 0.02 μ V equivalent voltage change). However, the absolute accuracy of the temperature as determined from the platinum thermometer resistance is limited to about one part in 10^5 (e.g., 3 mK at 300 K) by the accuracy of the standard resistor calibration and the accuracy of the resistance versus temperature calibration of the thermometer. The accuracy to which temperature intervals can be determined is limited by the smoothness of the thermometer calibration (1 part in 10^4 or better) or by the 0.1 mK resolution, whichever is greater.

With the germanium thermometer, 0.1 mK is readily resolved (typically a 0.1 μ V equivalent voltage change). The accuracy of absolute temperatures and of temperature intervals again is limited by the thermometer calibration and smoothness, respectively. These limits are about 1 mK for T and 0.1 mK for ΔT . The accuracy of the standard resistors is not a limitation with the germanium thermometry. The sample thermometry did not contribute significantly to the error in the calculated values of the thermal expansion coefficient.

The temperature of the cell is monitored using the sensors which are associated with the cell temperature controller. A block diagram of this ac-bridge temperature controller (ACTC) is given in Figure 8. A carbon resistor (Speer, $\frac{1}{2}$ watt, $470 \Omega \pm 10\%$ at room temperature, 925Ω at 4.2 K) is used for cell temperatures below 55 K, and a miniature platinum resistance thermometer (Minco, 100Ω at 273 K) is used for higher cell temperatures. The sensor resistance is compared to a reference resistance using the ac bridge. The reference resistance is the sum of a decade box setting (General Radio, type 1434-X, S/N-1344, 0.1Ω least count) and a separate 0 - 0.1Ω vernier. The bridge off-balance is applied to the input of a phase-sensitive lock-in null detector of local design and construction, including a built-in oscillator. The resulting dc output of the detector is fed to an integral/proportional/differential controller (Leeds and Northrup, M-Line Series 71, model C1; current-adjusting type (C.A.T.) controller). The C.A.T. output in turn drives a programmable constant voltage power supply which feeds the cell heater bands. The absolute temperature of the cell could be determined to within 1% with the carbon sensor below

Figure 8. A block diagram of the cell temperature controller used in the present work. This is the subsystem labeled ACTC in Figure 3.

55 K, and within 0.5 K with the platinum thermometer above 55 K. The precise temperature of the cell need not be known for the data analysis as long as the temperature is constant during the data acquisition, so only a crude calibration of the sensors was made with respect to the sample thermometers (see below). Sufficient sensitivity was used in the temperature sensing system of the ACTC to hold the cell temperature stable to better than 1 mK. This system has been used on other cryostats with a typical stability of ± 0.1 mK, and it is reasonable to assume this level of stability in the present experiment.

Differential thermocouples were used to monitor the temperature difference between the sample and cell ("S/C", points E and D, respectively, in Figures 3, 4, and 5), between the top of the cell and the bottom of the support post heater ("C/P", points A and B, respectively), and between the top of the cell and the top of the vacuum can ("C/C", points A and C, respectively). The C/P and C/C differential thermocouples, and initially the S/C differential thermocouple, were a gold-iron alloy (Au + 0.03% Fe) versus copper. The S/C differential thermocouple later was changed to a slightly less sensitive gold-iron versus silver normal (Ag + 0.02% Cu) combination to eliminate the copper wire heat leak from the sample to the cell. The S/C differential thermocouple was used as a zero temperature difference detector in the calibration of the ACTC sensors with respect to the sample thermometry. The thermocouple voltages were measured by a Keithley model 155 microvoltmeter with its output displayed on one pen of a second dual-pen chart recorder (see Figure 3). The second pen of this

recorder displayed the quadrature off-balance signal from the capacitance bridge.

The experimental linear thermal expansion data for copper and aluminum are presented in the next chapter and compared graphically to the results of others. A discussion of sources of errors concludes the chapter.

CHAPTER III. RESULTS

The brief descriptions of the experimental procedure and data analysis which are given below are followed by a presentation of the results of the thermal expansion coefficient measurements on copper and aluminum. The experimental data are presented in the form of percentage plots of the deviation $(\alpha - \alpha_{\text{calc}})/\alpha_{\text{calc}}$ for each fit range, where α_{calc} is the value of the thermal expansion coefficient as calculated from the appropriate fit coefficients. The fit coefficients are listed and smoothed values of the thermal expansion coefficients of copper and aluminum are tabulated in the accompanying tables. One or two representative curves also are included on the deviation plots to show how the results of others differ from the present results. The deviations of all other measurements mentioned in Chapter I are shown in a single plot (one each for copper and aluminum) for the entire temperature range. The results are further discussed in Chapter IV.

Experimental Procedure

After the sample was wrapped with the heater wires and thermometer anchoring leads (as described in the previous chapter), the platinum and germanium thermometers were inserted into their respective holes using silicone vacuum grease for increased thermal contact, and the thermometer terminals were soldered to their appropriate anchoring leads. The sample was placed on the glass spacers on the bottom capacitor plate, and raised into the cell as the wires were routed through the cell wall hole. The sample and reference capacitances were checked; and, when satisfactory,

the electrical connections to the cell tie points were made. The capacitances and electrical circuits were checked before and after the vacuum can was soldered into place. The apparatus was helium leak-tested at room temperature and with the vacuum can at liquid nitrogen temperature, and when leak tight was placed in the dewar system. (see Figure 2).

Preliminary to the acquisition of the copper data, the apparatus was checked for systematic effects due to possible temperature gradients in the capacitance cell. Thermal expansion measurements were made above room temperature with the vacuum can at room temperature, and above liquid nitrogen temperature with the vacuum can immersed in liquid nitrogen, both with and without the support post heater energized. Exchange gas was introduced into the vacuum can so that the heater powers required to hold temperatures were doubled, presumably enhancing any thermal gradient effects; additional thermal expansion measurements then were made. Gradient effects, if any, were less than 0.1% in the thermal expansion coefficient.

During the acquisition of the copper and aluminum data, measurements were made with the vacuum can at 4.2 K (liquid helium) to sufficiently high cell and sample temperatures to overlap with measurements which were made with the vacuum can at 50 K (solid nitrogen) or at 77 K (liquid nitrogen). Similar overlaps were made with the vacuum can at 77 K and near room temperature. Despite the drastically different cell and post heater power levels, the overlap points show no systematic differences as large as 0.1%. The thermal environment of the cell (vacuum can temperature and post heater power) never was changed during any individual

thermal expansion measurement in the present work. If any thermal gradients in and length distortions of the cell existed, their effects should cancel to first order when α is calculated, as long as they were almost constant during the measurements for the calculation [see also the discussion preceding Equation (1-44)].

An individual determination of a thermal expansion coefficient at a given temperature was carried out in the following manner. The cell temperature was stabilized and automatically maintained constant by the ACTC. The sample temperature was stabilized manually by adjustment of its heater current. Temperature stability was monitored by observing the chart recorder traces for the sample thermometer and the various differential thermocouples. The thermometer (PT or GE) current was checked, the thermometer resistance was determined, and the sample temperature was calculated from the thermometer calibration tables. The sample (C_s) and reference (C_r) capacitances were measured and recorded. Corrections to the last digit or two were obtained from the chart recorder traces. The recorder amplifier gains had been set so that the major divisions on the charts were calibrated in microvolts for the thermometry and in 10^{-4} to 10^{-6} picofarads for the capacitance. The three differential thermocouple voltages also were recorded.

The sample temperature then was raised by the desired temperature increment ΔT and stabilized, while the cell temperature was held constant by the ACTC. The temperature increments used were typically $T/10$ at low temperatures, increasing to 5, 10, or 20 K at higher temperatures. The new sample temperature T' and the new capacitance readings C_s' and C_r' were

recorded, as well as the differential thermocouple voltages. The thermal expansion coefficient at the average temperature, $T_{\text{avg}} = \frac{1}{2}(T + T')$, then was calculated from the two sets of capacitance readings and sample temperature (see below for calculation details). The temperature of the sample then could be raised by another increment, new readings taken, and the thermal expansion coefficient calculated for a new average temperature, still keeping the temperature of the cell constant.

This procedure was continued until the cell heater current as determined by the ACTC had been reduced nearly to zero. Typically, temperature differences ($T_{\text{sample}} - T_{\text{cell}}$) could be achieved which were comparable to the difference between the cell and vacuum can temperatures. Large differences ($T_s - T_c$) did not introduce any systematic errors compared to data points at the same T_s but with different T_c . Negative temperature increments also were used, starting with the sample much warmer than the cell, and then cooling it in steps. This occasionally was more convenient at low temperatures ($T < 35$ K); and no systematic differences were observed between warming and cooling measurements. After a series of measurements, the reference resistance of the ACTC was changed and the controller stabilized the cell temperature at a new value to begin another series.

The time required to change the temperature of the sample for a thermal expansion measurement ranged from a few minutes below 10 K to about an hour above 200 K, depending on the magnitude of the temperature increment, the heat capacity of the 0.93-kg copper or 0.28-kg aluminum sample, and the limitations on available heater power. The more massive

cell (1.44 kg) required more time to change its temperature, in part since less heater power was available. The time required to stabilize temperatures after a change was less than but comparable to the time consumed in the change.

Analysis of Data

Each value for the thermal expansion coefficient was calculated from two sets of capacitance and sample temperature readings (C_s, C_r, T) and (C'_s, C'_r, T'). The change in the length of the sample ΔL_s is obtained from the capacitance measurements via Equations (I-41) through (I-44) as

$$\Delta L_s = \frac{\epsilon_o A_s}{C_s C'_s} \Delta C_s + \frac{\epsilon_o A_r}{C_r C'_r} \Delta C_r, \quad (III-1)$$

where ϵ_o is the permittivity of free space, A_s and A_r are the sample and reference capacitor effective plate areas, and $\Delta C = C' - C$. The plate areas were determined from room temperature diameter measurements made with a travelling microscope. To the first approximation, the effective area of the plates extends half way across the insulation gap; higher order corrections due to field perturbations are very difficult to determine, but are much smaller than 0.1% (69). Several diameter measurements were made at 45° angular positions and the diameter squared results averaged to obtain $\epsilon_o A_s = 0.25443$ pF-cm and $\epsilon_o A_r = 0.25180$ pF-cm, each with a root-mean-square deviation of 0.05%.

Substitution of Equation (III-1) into Equation (I-3) gives

$$\bar{\alpha}(T_{avg}) = \frac{(\epsilon_o A_s / L_s)}{C_s C'_s} \left(\frac{\Delta C_s}{\Delta T} \right) + \frac{(\epsilon_o A_r / L_s)}{C_r C'_r} \left(\frac{\Delta C_r}{\Delta T} \right) \quad (III-2)$$

for the calculated thermal expansion coefficient. In practice, the room

temperature values of $(\epsilon_o A_s/L_s)$ and $(\epsilon_o A_r/L_s)$ were first used to calculate an $\alpha_o(T_{avg})$. Then a multiplicative correction, the same for both terms of Equation (III-2), was applied to α_o for the change in the areas (A_s, A_r) and sample length (L_s) between room temperature and T_{avg} :

$$\frac{A(T_{avg})}{L(T_{avg})} = \frac{A_o}{L_o} \frac{(1 + \delta r/r_o)^2}{(1 + \delta L/L_o)} \quad , \quad (III-3)$$

Where the subscript "o" indicates the room temperature measured values, and where $\delta r/r_o$ and $\delta L/L_o$ are obtained from the integrated thermal expansion. Note that with the aluminum sample, L_s must be corrected in terms of aluminum and the capacitance plate areas in terms of copper, whereas with the copper sample the correction is all for copper. The multiplicative correction reached approximately -0.35% at low temperatures (A/L decreases slowly with temperature). Technically, the areas should be corrected to the cell temperature, but the error introduced by correcting to the sample average temperature (T_{avg}) is negligible.

In summary, first $\alpha_o(T_{avg})$ was calculated from the measured (T, C_s, C_r) and (T', C_s', C_r') and room temperature values of A_s, A_r , and L_s in Equation (III-2). Then a multiplicative correction for dimensional changes was made to obtain $\bar{\alpha}(T_{avg})$, Equation (III-2). Finally, a small correction (generally of the order of 0.1%) for the use of finite temperature intervals was added if necessary to obtain $\alpha(T_{avg})$. See Appendix B for details of the finite temperature interval corrections.

The experimental values for the thermal expansion coefficient then were fit with a power series in the temperature:

$$\alpha(T) = \sum A_n T^n \quad (III-4)$$

with a computer least-squares fitting program. Data points which scattered more than two standard deviations from the smooth curves were discarded after initial fitting; except at low temperatures (under 15 K), very few points were discarded. In some cases, two points sharing a common set of T , C_s , and C_r values scattered by more than two standard deviations, one above and one below a smooth curve through the data. When this happened, the temperature intervals were combined for a single data point, bridging the presumably erroneous intermediate T , C_s , or C_r . These "combined interval" points are suitably noted in the data listings of Appendix A. The fit ranges were selected so that a fifth order polynomial in the temperature fit the data well, with five to ten points in each overlap region. The fit ranges overlap smoothly, well within the scatter of the data; the first and second derivatives also match well (see below). Third and fourth order fits always resulted in deviation plots, $(\alpha - \alpha_{calc})/\alpha_{calc}$, which had a systematic oscillation. The oscillations vanished with a fifth order fit, and there was no significant additional improvement with a sixth order fit.

Below 5 K for copper and 10 K for aluminum, the experimental data rose systematically above previous low temperature results (30, 31, 45) which are believed to be correct, and they often showed scatter which was well outside of nominal experimental accuracy. These points were not used in the least-squares fitting, and a possible explanation of the

abnormal behavior will be discussed in the section on sources of error. The experimental data points which were used in the various fits, and the unused low temperature points which do not scatter grossly from a smooth curve, are given in Appendix A. Tabulations of smoothed values of the linear thermal expansion coefficients of copper and aluminum are given in the following sections, along with the fit coefficients and deviation plots.

Copper

The thermal expansion coefficient data for copper from 325 K to 5.5 K were fit in four overlapping ranges: 325 K to 90 K, 110 K to 45 K, 55 K to 20 K, and 30 K to 5.5 K. The coefficients of the fit equations are given in Table 2, and when used in Equation (III-4), give the thermal expansion coefficient α in units of K^{-1} when the temperature T is expressed in kelvins. The eight significant figures which are given for each coefficient are sufficient to calculate $\alpha(T)$ beyond the experimental accuracy. The fit range and the useful range of each fit, the number of points in each fit, and the root-mean-square deviation (RMSD) of the data points used in each fit, are given with the corresponding set of coefficients. Table 3 is a tabulation of smoothed values of the linear thermal expansion coefficient of copper as calculated from the fit equations. Values are tabulated at temperatures sufficiently close so that linear interpolation introduces errors of less than two RMSD from the smooth fits. One more significant figure is given (for interpolation purposes) than is nominally justified by experimental

Table 2. Least-squares fit coefficients for the copper thermal expansion coefficient data.

Fit range: 5.5 - 30 K	$A_0 = 5.1703067 \times 10^{-9}$
Useful range: 5 - 25 K ^a	$A_1 = -2.9885049 \times 10^{-9}$
RMSD = 0.59% for 44 data points.	$A_2 = 7.4727881 \times 10^{-10}$
	$A_3 = -5.1947821 \times 10^{-11}$
	$A_4 = 3.6753422 \times 10^{-12}$
	$A_5 = -4.7643946 \times 10^{-14}$
Fit range: 20-55 K	$A_0 = -5.1035251 \times 10^{-7}$
Useful range: 25-50 K	$A_1 = 1.1273627 \times 10^{-7}$
RMSD = 0.09% for 23 data points.	$A_2 = -9.5015347 \times 10^{-9}$
	$A_3 = 3.9282915 \times 10^{-10}$
	$A_4 = -5.7295663 \times 10^{-12}$
	$A_5 = 2.9424260 \times 10^{-14}$
Fit range: 45-110 K	$A_0 = 7.8669295 \times 10^{-6}$
Useful range: 50-100 K	$A_1 = -7.0659758 \times 10^{-7}$
RMSD = 0.06% for 23 data points.	$A_2 = 2.3812023 \times 10^{-8}$
	$A_3 = -3.1035898 \times 10^{-10}$
	$A_4 = 1.9328121 \times 10^{-12}$
	$A_5 = -4.7699183 \times 10^{-15}$
Fit range: 90-325 K	$A_0 = -1.1286262 \times 10^{-5}$
Useful range: 100-325 K	$A_1 = 4.1318723 \times 10^{-7}$
RMSD = 0.04% for 24 data points.	$A_2 = -2.7945212 \times 10^{-9}$
	$A_3 = 1.0259471 \times 10^{-11}$
	$A_4 = -1.9528359 \times 10^{-14}$
	$A_5 = 1.5129108 \times 10^{-17}$

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^aExtrapolation to 5 K.

Table 3. Smoothed values of the linear thermal expansion coefficient of copper calculated with the fit coefficients of Table 2.

T (K)	α (K ⁻¹)	T (K)	α (K ⁻¹)	T (K)	α (K ⁻¹)
5 ^a	$4.5_6 \times 10^{-9}$	27	$7.16_5 \times 10^{-7}$	80	8.370×10^{-6}
6	7.3_1	28	8.05_0	85	8.978
7	$1.10_7 \times 10^{-8}$	29	9.00_0	90	9.545
8	1.60	30	1.001×10^{-6}	95	10.070
9	2.22	32	1.219	100	10.550
10	3.01	34	1.459	(change fit)	
11	3.97	36	1.718	105	10.985
12	5.15	38	1.993	110	11.391
13	6.58	40	2.283	115	11.765
14	8.28	42	2.585	120	12.111
15	1.030×10^{-7}	44	2.895	130	12.725
16	1.268	46	3.213	140	13.251
17	1.545	48	3.536	150	13.704
18	1.864	50	3.862	160	14.095
19	2.229	(change fit)		170	14.437
20	2.644	52	4.191	180	14.738
21	3.112	54	4.521	190	15.004
22	3.635	56	4.849	200	15.243
23	4.217	58	5.175	220	15.655
24	4.86_0	60	5.497	240	16.000
25	5.56_5	65	6.279	260	16.292
(change fit)		70	7.021	280	16.541
26	6.33_5	75	7.718	300	16.759
				320	16.960

^aExtrapolated just below lowest fit range.

accuracy. The change over points from one set of fit coefficients to another are indicated in the tabulations.

Deviations of the experimental data from the fitted curves (α_{calc}) are shown in Figures 9, 10, 11, and 12. The different plotting symbols (solid circles, open squares, and open triangles) represent different data "runs" (1, 2, and 3, respectively). The data points are listed in Appendix A, the points belonging to each run are differentiated there. Between the runs, the apparatus was warmed to room temperature, removed from the dewar system for minor modifications, returned to the dewar system, and cooled down again. The data from different runs overlap considerably and show no systematic differences. Also plotted on the figures are the deviations of the smoothed results of Hahn (NBS) (1) and Rubin et al. (33) above 20 K, and White and Collins (31) and McLean et al. (30) below 35 K. The deviations of these and all the other measurements on copper mentioned in Chapter I are shown in Figure 13 for the entire temperature range.

The agreement above 50 K between the present results and the 1954 results of Rubin et al. (33) (RUBIN in Figures 9 and 10, and RAJ in Figure 13) is surprisingly good. The poorer agreement with the more recent (1970) results of Hahn (for NBS Standard Reference Material 736 - Copper) also is evident. The smoothness of the present results in the overlap regions of the fit ranges can be judged through comparisons of the deviations of common data points on different plots. The agreement in the magnitude of α in the overlap regions is within the scatter of

Figure 9. Deviation of the present experimental data for copper and of the results of Hahn (1) and Rubin et al. (33) from the smooth representation of the data for the temperature range 90 K to 325 K. The different plotting symbols are explained in the text.

Figure 10. Deviation of the present experimental data for copper and of the results of Hahn (1), Rubin et al. (33), and White and Collins (31) from the smooth representation of the data for the temperature range 45 K to 110 K. The plotting symbols are as in Figure 9.

Figure 11. Deviation of the present experimental data for copper and of the results of Hahn (1), White and Collins (31), and Case (Cu-3) of McLean *et al.* (30) from the smooth representation of the data for the temperature range 20 K to 55 K. The plotting symbols are as in Figure 9.

Figure 12. Deviation of the present experimental data for copper and of the results of White and Collins (31) and Case (Cu-3) of McLean *et al.* (30) from the smooth representation of the data for the temperature range 5 K to 30 K. The plotting symbols are as in Figure 9.

Figure 13. Comparison of previous work on copper with the smoothed present results (α_{calc}). Note the change of horizontal scale at 40 K. The references are: WC - 31, MSC - 30, CMW - 25, STG - 27, CS - 26, AG - 42, CY - 41, BW - 40, FHH - 38, SB - 35, BP - 34, RAJ - 33, H - 1, LS - 39, LN - 36, and RMHM - 37. PBG - 29 is off-scale (negative).

the data; the first derivative values ($d\alpha/dT$) compare within 0.5 to 2%, and the second derivative values agree within 2 to 5%, with the worst disagreement in the overlap around 25 K. (Figures 11 and 12).

Figure 13 clearly shows that for most of the other measurements, the worst disagreements are at the low temperature ends of the individual measurements where the various techniques suffer from inadequate sensitivity, and at temperatures below 60 K in general where high sensitivity is needed. Some of the discrepancies at low temperatures for the older results may be due to temperature scale or thermometry problems in addition to insufficient sensitivity.

Aluminum

The linear thermal expansion data for aluminum from 330 K to 11 K also were fit in four overlapping ranges: 330 K to 100 K, 150 K to 50 K, 85 K to 30 K, and 35 K to 11 K. The fit coefficients, etc., are given in Table 4, and smoothed values are tabulated in Table 5, with the same format as for copper.

Deviations of the experimental data, listed in Appendix A, from the fitted curves (α_{calc}) are shown in Figures 14, 15, 16, and 17. All of the aluminum data was taken during one "cool down" of the apparatus and the different plotting symbols represent a convenient (for analysis) partitioning of the data which were taken in the order solid circles, open squares, and open triangles, chronologically. Also plotted on these figures are the smoothed results of Altman *et al.* (46) and of Collins, White, and Swenson (45). The relative (versus copper) expansion

Table 4. Least-squares fit coefficients for the aluminum thermal expansion coefficient data.

Fit range: 11-35 K ^a	$A_0 = 3.2661408 \times 10^{-8}$
Useful range: 10-32 K ^a	$A_1 = -1.2811084 \times 10^{-8}$
RMSD = 0.40% for	$A_2 = 2.2050497 \times 10^{-9}$
24 data points.	$A_3 = -1.3386148 \times 10^{-10}$
	$A_4 = 5.0983621 \times 10^{-12}$
	$A_5 = -5.4014065 \times 10^{-14}$
Fit range: 30-85 K	$A_0 = 2.6606098 \times 10^{-6}$
Useful range: 32-75 K	$A_1 = -2.4747887 \times 10^{-7}$
RMSD = 0.10% for	$A_2 = 7.3618080 \times 10^{-9}$
18 data points.	$A_3 = -3.1584155 \times 10^{-11}$
	$A_4 = -2.6986328 \times 10^{-13}$
	$A_5 = 1.9378275 \times 10^{-15}$
Fit range: 55-150 K	$A_0 = 3.2437821 \times 10^{-7}$
Useful range: 75-130 K	$A_1 = -1.6965659 \times 10^{-7}$
RMSD = 0.04% for	$A_2 = 7.8155998 \times 10^{-9}$
20 data points.	$A_3 = -7.7108957 \times 10^{-11}$
	$A_4 = 3.3197763 \times 10^{-13}$
	$A_5 = -5.4460787 \times 10^{-16}$
Fit range: 100-330 K	$A_0 = -1.5512702 \times 10^{-5}$
Useful range: 130-330 K	$A_1 = 4.8387753 \times 10^{-7}$
RMSD = 0.04% for	$A_2 = -2.8899789 \times 10^{-9}$
22 data points.	$A_3 = 9.8370004 \times 10^{-12}$
	$A_4 = -1.7971507 \times 10^{-14}$
	$A_5 = 1.3762062 \times 10^{-17}$

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^aExtrapolation to 10 K.

Table 5. Smoothed values of the linear thermal expansion coefficient of aluminum calculated with the fit coefficients of Table 4.

T (K)	α (K ⁻¹)	T (K)	α (K ⁻¹)	T (K)	α (K ⁻¹)
10 ^a	3.68×10^{-8}	(change fit)		95	11.457×10^{-6}
11	4.63	34	1.243×10^{-6}	100	12.157
12	5.74	36	1.483	110	13.433
13	7.02	38	1.745	115	14.011
14	8.50	40	2.027	120	14.553
15	1.029×10^{-7}	42	2.326	130	15.539
16	1.214	44	2.642	(change fit)	
17	1.436	46	2.971	140	16.415
18	1.690	48	3.311	150	17.191
19	1.978	50	3.662	160	17.881
20	2.305	52	4.021	170	18.499
21	2.673	54	4.386	180	19.053
22	3.087	56	4.755	190	19.554
23	3.549	58	5.127	200	20.008
24	4.063	60	5.502	220	20.802
25	4.63 ₀	65	6.436	240	21.473
26	5.25 ₅	70	7.354	260	22.051
27	5.94 ₀	75	8.245	280	22.559
28	6.68 ₅	(change fit)		300	23.020
29	7.49 ₀	80	9.105	320	23.460
30	8.36 ₀	85	9.930		
32	1.028×10^{-6}	90	10.714		

^aExtrapolated just below lowest fit range.

Figure 14. Deviation of the present experimental data for aluminum and of the results of Altman *et al.* (46) and White of Collins *et al.* (45) from the smooth representation of the data for the temperature range 100 K to 330 K. White's value at 283 K has been corrected for his copper reference (see the text). The plotting symbols are explained in the text.

Figure 15. Deviation of the present experimental data for aluminum and of the results of Altman *et al.* (46) and White of Collins *et al.* (45) from the smooth representation of the data for the temperature range 50 K to 150 K. White's values for 55 K to 85 K have been corrected for his copper reference (see the text). The plotting symbols are as in Figure 14.

Figure 16. Deviation of the present experimental data for aluminum and of the results of Altman *et al.* (46) and Collins, White, and Swenson (45) from the smooth representation of the data for the temperature range 30 K to 85 K. W&S is the average of the separate results of White and Swenson (see the text). The plotting symbols are as in Figure 14.

Figure 17. Deviation of the present experimental data for aluminum and of the results of Collins, White, and Swenson (45) from the smooth representation of the data for the temperature range 11 K to 35 K. W&S is the average of the separate results of White and Swenson (see the text). The plotting symbols are as in Figure 14.

Figure 18. Comparison of previous work on aluminum with the smoothed present results (α_{calc}). Note the change of horizontal scale at 40 K. The references are: CWS - 45, AG - 42, FHH - 38, G - 47, HAJ - 48, BP - 34, RMHM - 37, and ARJ - 46. Off-scale as indicated are CS - 26 and W - 22.

results of White in Collins et al. for 50 K to 90 K and at 283 K have been corrected for the deviations of their reference copper expansion values (Hahn at 283 K, and nominally Rubin for 50 to 90 K, see Figure 10) from the present results. The low temperature curve "W & S" in Figures 16 and 17 is the averaged result of White's capacitance dilatometer measurements and Swenson's variable transformer dilatometer results; they do not differ significantly in the temperature range plotted. As with copper, the deviations of these and the other results for aluminum mentioned in Chapter I (significantly fewer in number) are shown in Figure 18 for the entire temperature range.

The agreement between the present results and the 1955 work of Altman et al. (46) is not as good as for copper, but still within the combined error bars above 55 K. The excellent agreement with the results from Collins et al. (45), particularly when their results at higher temperatures are corrected for the deviations of their copper reference, strongly suggests that there are no significant systematic errors in the present measurements.

Sources of Error

Errors in the calculation of the linear thermal expansion coefficient from the raw temperature and capacitance data using Equation (III-2) may arise from individual errors in (i) the sample length L_s , (ii) the capacitor plate areas A_s and A_r , (iii) the temperatures, both T and ΔT , and (iv) the capacitances and capacitance changes C_s , C_r , ΔC_s , and ΔC_r .

The sample and cell lengths were measured with a micrometer and are consistent with lengths as calculated from measured capacitances to better than 0.005% (see "Characterization of Samples" in the previous chapter). The plate areas were measured with a standard deviation of 0.05% (see "Analysis of Data" in this chapter). In correcting the factors ($\epsilon_0 A/L$) of Equation (III-2) from room temperature to the data temperature, an additional error of about 0.01% could be introduced. Thus the factors ($\epsilon_0 A_S/L_S$) and ($\epsilon_0 A_R/L_S$) could contribute at most a systematic error of the order of 0.05%, but should not contribute to the scatter of the data.

The data scatter is the result of errors in the measurement of the sample temperature and the capacitances, and uncertainties due to instabilities of the cell temperature or length aberrations due to temperature gradients. The accuracy of the sample temperature and the temperature interval measurements was discussed earlier (see "Thermometry" in Chapter II), with the conclusion that ΔT is known to ± 0.1 mK or $\pm 0.01\%$, whichever is larger. The cell temperature controller also was discussed earlier (see "Thermometry", also) and is believed to be stable to ± 0.1 mK at least at lower temperatures, and maybe slightly worse (to ± 1 mK at most) above 100 K. Since cell temperature fluctuations may be expressed as additive errors to ΔT , a reasonable upper limit of the total error in ΔT is ± 0.2 mK or $\pm 0.02\%$ whichever is larger. There is also the possibility of small (at most 1-2 mK) temperature gradients in the cell when operated at high temperatures (say, above 200 K), which also may be translated into a negligible contribution to the total error in ΔT .

The greatest source of error at low temperatures, and a major source at higher temperatures, stems from the capacitance readings. The 100 pF standard capacitance (according to the calibration certificate supplied by General Radio) is known to better than 0.01%, the 0.1 pF standard to 0.1%. A direct measurement of the ratio (100 pF/0.1 pF) indicated that the 0.1 pF standard may be high (in a relative sense) by almost 0.1%. The 0.1 pF standard was used only for the 10^{-5} pF and smaller decades, so the accuracy of the absolute value of the capacitances is determined by the 100 pF standard. The ratio transformers are accurate to 10 ppm or better and hence contribute no significant error to the capacitance measurements.

The accuracy of the capacitance changes ΔC_s and ΔC_r is limited by a combination of the resolution of the bridge (particularly at low temperatures) and the accuracies of the standards. To estimate the (maximum) resolution-caused error, assume that each capacitance can be read to a precision of δC (i.e. $\pm \frac{1}{2} \delta C$); then each ΔC is known to $\pm \delta C$ and Equation (III-2) may be rewritten as

$$\alpha \pm \delta\alpha = A(\Delta C_s \pm \delta C) + B(\Delta C_r \pm \delta C). \quad (\text{III-5})$$

Since A and B are approximately equal, this reduces to

$$\frac{\pm \delta\alpha}{\alpha} \approx \frac{\pm 2 \delta C}{\Delta C_s + \Delta C_r}, \quad (\text{III-6})$$

giving the maximum relative error in the calculated thermal expansion coefficient due to limited resolution. The magnitude of this possible

error is shown in Table 6, for the copper data points at 2.2 K, 5 K, and 10 K; the behavior for aluminum is similar. Limited resolution is the major source of random error and scatter in the data below 10 K. At higher temperatures, the sensitivity of the capacitance bridge detector was such that resolution error amounted to 0.01% or so, and the residual scatter in the data is due to a combination of all the aforementioned sources of error.

Table 6. Maximum resolution-caused error - sample values for copper.

T_{avg}	ΔT	$\Delta C_s + \Delta C_r$	δC	$\delta \alpha / \alpha$
2.224 K	0.548 K	15×10^{-7} pF	10^{-7} pF	13.3%
5.000 K	1.000 K	109×10^{-7} pF	10^{-7} pF	1.8%
10.001 K	0.998 K	935×10^{-7} pF	10^{-7} pF	0.2%

As was mentioned previously, the copper data below about 5 K and the aluminum data below about 10 K deviate systematically above the results of other recent low temperature measurements (30, 31, 45) which are believed to be correct. This is particularly severe for aluminum where the present data are 10% high around 7 K and 15% high around 4 K. The data could be fit with an expression of the form $\alpha = AT + BT^3$, Equation (1-40), only if an abnormally high electronic contribution is used. With the aluminum sample there was also an apparently constant background drift in the measured capacitances of the order of 10^{-7} pF/min (nominally

equal and opposite drifts for C_s and C_r) which interfered with the acquisition of the low temperature data. At a given temperature, C_s and C_r were monitored alternately and a line was drawn through each set of chart recorder traces so as to give values for C_s and C_r at the same point in time. The "enhanced" expansion and the drift were significantly smaller for the copper sample.

At first, anomalous expansion of the glass spacers on which the sample rests was considered as the cause of the drift. With the sample and cell temperatures constant, C_s drifted up in value and C_r down, as if the sample was rising and the spacers expanding; 10^{-7} pF/min translates into about 0.06 Å/min for the aluminum sample. A mass spectrographic analysis of the glass showed it to be consistent with "soda-lime" glass for which White (70) has measured the thermal expansion coefficient at low temperatures. This glass has a negative thermal expansion below 11 K, with a peak of $-7 \times 10^{-9} \text{ K}^{-1}$ around 8 K. The spacers for the aluminum sample were about 0.7 mm thick, so to cause the capacitance drift, the average temperature of the spacers would have to drift by at least 1 K/min which is impossible. Only near room temperature could the behavior of the reference capacitor be "explained" by thermal expansion of the glass spacers.

Since considerably more helium exchange gas was used in the vacuum can when cooling the apparatus to 4.2 K with the aluminum sample than with the copper sample, the possibility of an adsorbed layer (or layers) of helium on the sample, cell, and spacer surfaces was considered. Films on the spacer surfaces could simulate anomalous expansion of the glass.

The enhanced dielectric constant of helium layers on the capacitor plates could cause the low temperature capacitances and hence the measured thermal expansion values to be high, but not by the observed 10-15%. The effects would diminish at higher temperatures as the adsorbed layer(s) evaporated. However, when the apparatus with the aluminum sample was cooled from room temperature to 4.2 K without any exchange gas, the drift and enhanced expansion remained, and the theory of the adsorbed helium layer(s) was abandoned.

An alternate theory for both the drift and enhanced expansion involves infinitesimal tipping of the sample. When the sample is tipped through an angle $\delta\theta$, the reference capacitor gap L_{gr} , measured along the axis through the centers of the capacitor plates in the cell ends, is increased by $\delta L_{gr} \approx R \sin \delta\theta \approx R \delta\theta$, where R is the effective tipping radius of the base of the sample. The effective length of the sample along the same axis is $L_s' = L_s / \cos \delta\theta$, so the length is increased by $\delta L_s \approx L_s (\delta\theta/2)^2$ and hence the sample capacitor gap L_{gs} is decreased by $\delta L_{gs} = -\delta L_{gr} - \delta L_s$. With $\delta\theta \ll 1$, δL_s is negligible compared to δL_{gr} , so $\delta L_{gs} \approx -\delta L_{gr}$ and the capacitance drifts in opposite directions are anticipated. Since $C = \epsilon_0 A / L_g$, the tipping rate calculated from the observed capacitance drift ($dC_r / dt \approx -10^{-7}$ pF/min) is found to be

$$\frac{d\theta}{dt} \approx -\frac{\epsilon_0 A_r}{RC_r} \frac{dC_r}{dt} \approx 4 \times 10^{-10} \text{ rad/min}, \quad (III-7)$$

which is exceedingly small. (The low temperature values $C_s = 5.77$ pF,

$C_r = 6.42 \text{ pF}$, $\epsilon_0 A_s = 0.254 \text{ pF} \cdot \text{cm}$, $\epsilon_0 A_r = 0.251 \text{ pF} \cdot \text{cm}$, $R \approx 1.5 \text{ cm}$, and $L_s \approx 10.2 \text{ cm}$ for aluminum are used in the calculations.)

For the thermal expansion coefficient to be enhanced by $\delta\alpha/\alpha = 10\%$ at 5 K, Equation (III-6) indicates that a capacitance shift $\delta C_s + \delta C_r$ of about $+10^{-6} \text{ pF}$ must occur when the sample is heated, or -10^{-6} pF when cooled, by 1 K. Since

$$\begin{aligned} \delta C_s + \delta C_r &= - (C_s^2 / \epsilon_0 A_s) \delta L_{gs} - (C_r^2 / \epsilon_0 A_r) \delta L_{gr} \\ &\approx (C_s^2 / \epsilon_0 A_s - C_r^2 / \epsilon_0 A_r) R \delta\theta + (C_s^2 / \epsilon_0 A_s) L_s (\delta\theta/2)^2 \\ + 10^{-6} \text{ pF} &\approx (-50 \text{ pF}) \delta\theta + (334 \text{ pF}) (\delta\theta)^2, \end{aligned} \quad (\text{III-8})$$

a tipping of -2×10^{-8} radians (total tip decreased) is sufficient for the 10% enhancement. Differential expansion between the three glass spacers would tip the sample, but as was noted above, the low temperature thermal expansion coefficient of glass is much too small to explain the observed capacitance shifts or drifts.

A more probable cause of sample tipping is the torque exerted on the sample by the electrical leads between the sample and cell. For the copper sample, these leads were a mixture of four #38 copper and four #36 manganin (thermometry), three #30 manganin (heater), and two #36 thermocouple wires. To guard against the leads touching the cell or vacuum can, lengths of teflon sleeving were placed over the wires (two pieces for the eight thermometry leads, one for each heater lead, and one over the thermocouple leads). For the aluminum sample, the

thermometer and heater leads were all #30 manganin each in its own teflon sleeve. It is postulated that the differential thermal expansion between the stiff (at low temperatures) teflon sleeve and wire caused the combination to flex, exerting a force on the sample. The force would vary (probably inversely) with temperature as the effective spring constant changes. With the heavier wires, each in its own teflon sleeve, the tipping of the lighter aluminum sample would be significantly greater than for the copper sample. This correlates with the higher temperature (10 K) at which the effect becomes noticeable for aluminum, versus 5 K for copper. The flexing of the "spring" is probably a relaxation process, the capacitances should drift with time, and indeed they did. The drift was monitored for one twenty hour stretch with constant sample and cell temperatures (each at 6.0 K), and only a slight decrease in drift rate was observed, indicating a time constant of at least several days for the relaxation process.

Heating the sample would raise the equilibrium temperature of the wires and sleeving, probably reducing their effective spring constant, thus reducing the tipping force and the total tip, and vice versa when the sample is cooled, in agreement with the sign of the result calculated above. Thermal equilibrium in the wires and sleeving should lag behind thermal equilibrium in the sample, and indeed this may have been observed: When the temperature of the sample was raised, C_s increased nominally at first as the sample expanded; but as the sample temperature was re-stabilized, C_s "relaxed" back down partially as would be expected if the

tipping of the sample was reduced. In thermal expansion measurements made with negative temperature increments, the cooling was done too slowly to separate tipping effects from actual sample contraction effects. The magnitude of the tipping is such that even though it probably existed at all temperatures, it only could affect the measurements at low temperatures where the thermal expansion is small. The effects of non-parallel plates is several orders of magnitude smaller than the δL_g effects with $\delta\theta$ values this small. It is unfortunate that time did not permit the remounting of the aluminum sample without the teflon sleeving on the wires in order to verify this tipping theory.

In summary, the values of the linear thermal expansion coefficients of copper and aluminum as given by the smoothed fit relations are believed to have an accuracy comparable to the scatter of the data: $\pm 0.1\%$ above 50 K, decreasing to $\pm 0.5\%$ near 20 K and to about $\pm 1\%$ or so at 10 K. The useful temperatures ranges of the results are 5 K to 325 K for copper and 10 K to 330 K for aluminum. The comparison of the present results with the numerous other results in Figures 13 and 18 does not suggest the presence of any systematic errors as large as the above error limits.

2

CHAPTER IV. DISCUSSION AND CONCLUSIONS

The present results may be compactly described in terms of the lattice Grüneisen parameter, $\gamma^{\text{lat}}(T) = \alpha^{\text{lat}} 3B_T V / C_V^{\text{lat}}$ [Equation (I-9) and following], since good heat capacity data are available for copper (3, 24, 71) and reasonable data are available for aluminum (72-74). The low temperature behavior of $\gamma^{\text{lat}}(T)$ and the $T = 0$ limiting value γ_0 [Equation (I-21)] in general provide basic information about the anharmonicity of the interatomic potentials. The low temperature data in the present work are inadequate to estimate γ_0 . However, below 35 K, the present results overlap with the recent work of McLean, Swenson, and Case (30) and White and Collins (31) for copper and with Collins, White, and Swenson (35) for aluminum. Agreement is well within experimental accuracy for copper between 5 K and 35 K, and for aluminum between 10 K and 35 K. Therefore these results (30, 31, 35) have been assumed correct to show the behavior of $\gamma^{\text{lat}}(T)$ below the low temperature limits of the present results (copper - 5 K; aluminum - 10 K). The present data at the lowest temperatures rise systematically above these other results.

A plot of the lattice Grüneisen parameter

$$\gamma^{\text{lat}}(T) = \beta^{\text{lat}} B_T V / C_V^{\text{lat}} = \beta^{\text{lat}} B_S V / C_p^{\text{lat}} = 3\alpha^{\text{lat}} B_S V / C_p^{\text{lat}} \quad (\text{IV-1})$$

for copper is given in Figure 19; note that the temperature scale is logarithmic. The values of α^{lat} , B_S , V , and C_p^{lat} for the plotted γ^{lat}

points of Figure 19 are listed in the accompanying Table 7. The lattice contribution to the linear thermal expansion coefficient was calculated as $\alpha^{\text{lat}} = \alpha - \alpha^{\text{el}}$, where α is the measured total expansion coefficient and α^{el} is the electronic contribution as taken from the results of McLean et al. (30): $10^{10} \times \alpha^{\text{el}}(T) = (2.1 \pm 0.1 \text{ K}^{-2})T$. Values for the adiabatic bulk modulus B_S were taken from Overton and Gaffney (75); the molar volume V was calculated from the $T = 0$ value given by McLean et al. (30), $V_0 = 7.043 \text{ cm}^3/\text{mole}$, and the integrated values $(\Delta L/L)$ of the thermal expansion. The lattice heat capacity was calculated as $C_p^{\text{lat}}(T) = C_p - aT$ from the total C_p given by Furukawa et al. (3) assuming their electronic contribution $a = 0.695 \text{ mJ/mole} \cdot \text{K}^2$ for temperatures above 30 K; the C_p^{lat} values of Holste et al. (24) which assume $a = 0.692_6 \text{ mJ/mole} \cdot \text{K}^2$ were used below 30 K. A smooth curve may be readily drawn through the plotted points, and the residual scatter about the curve ($\pm 0.2\%$ at most) reflects the combined accuracy of the heat capacity data and the present thermal expansion data. The value $\gamma_0^{\text{elas}} = 1.73 (\pm 5\%)$ for the $T = 0$ elastic Grüneisen parameter [Equation (1-25) and following] was calculated from the elastic data of Daniels and Smith (76).

A plot of the lattice Grüneisen parameter $\gamma^{\text{lat}}(T)$ for aluminum is given in Figure 20; Table 8 lists the values of α^{lat} , B_S , V , and C_p^{lat} used to calculate the plotted γ^{lat} points. The lattice contribution α^{lat} to the total measured thermal expansion coefficient was calculated using the electronic contribution of Collins et al. (45), $10^{10} \times \alpha^{\text{el}}(T) = (9.3 \pm 0.1 \text{ K}^{-2})T$. The adiabatic bulk modulus B_S was taken from Kamm and Alers (77); the molar volume V was calculated from the $T = 0$ value given

Figure 19. The lattice Grüneisen parameter for copper as a function of temperature. The plotted points are those calculated in Table 7. The low temperature results are from White and Collins (31) and McLean *et al.* (30) along with their T=0 limiting value ranges. The T=0 elastic value γ_0^{elas} is calculated from Daniels and Smith (76).

Table 7. Data for the calculation of the lattice Grüneisen parameter for copper.

T (K)	α^{lat} ^a ($\times 10^{-6} \text{K}^{-1}$)	c_p^{lat} ^b (J/mole·K)	β_s ^c ($\times 10^{10} \text{N/m}^2$)	v ^d (cm^3/mole)	γ^{lat}
5	0.00348 ₇	0.00593 ₅	14.203	7.043	1.763
7	0.00956 ₅	0.01636	14.203	7.043	1.755
10	0.0279 ₀	0.04846	14.203	7.043	1.728
12	0.0489 ₂	0.08531	14.203	7.043	1.721
15	0.0994	0.1734	14.202	7.043	1.720
20	0.2601	0.4479	14.201	7.043	1.742
25	0.5511	0.9395	14.199	7.043	1.760
30	0.9944	1.667	14.196	7.043	1.789
35	1.578 ₆	2.614	14.193	7.044	1.811
40	2.274	3.712	14.190	7.044	1.837
50	3.851	6.119	14.181	7.045	1.886
60	5.484	8.553	14.170	7.046	1.920
70	7.006	10.81	14.158	7.048	1.940
85	8.960	13.68	14.137	7.051	1.957
100	10.52 ₉	15.94	14.115	7.054	1.973
120	12.08 ₅	18.17	14.081	7.058	1.983
150	13.67	20.14	14.027	7.064	1.991
200	15.20	22.49	13.927	7.077	1.998
250	16.10	23.61	13.820	7.094	2.006
300	16.70	24.25	13.708	7.115	2.015

^aCalculated using α^{el} from McLean et al. (30).

^bBelow 30 K from Holste et al. (24); above 30 K calculated from Furukawa et al. (3).

^cOverton and Gaffney (75).

^dCalculated from $V_0 = 7.043 \text{ cm}^3/\text{mole}$ from McLean et al. (30) using integrated values ($\Delta L/L$) of the thermal expansion.

Figure 20. The lattice Grüneisen parameter for aluminum as a function of temperature. The plotted points are those calculated in Table 8. The low temperature results are from Collins *et al.* (45) including their $T=0$ limiting value range.

Table 8. Data for the calculation of the lattice Grüneisen parameter for aluminum.

T (K)	α^{lat} ^a ($\times 10^{-6} \text{K}^{-1}$)	c_p^{lat} ^b (J/mole·K)	B_S ^c ($\times 10^{10} \text{N/m}^2$)	V ^d (cm^3/mole)	γ^{lat}
10	0.0274	0.0234	7.937	9.872	2.752
12	0.0462	0.0400	7.937	9.872	2.715
15	0.0879	0.0781	7.936	9.872	2.641
20	0.2118	0.1970	7.936	9.872	2.527
25	0.4397	0.4348	7.936	9.872	2.377
30	0.8079	0.8087	7.937	9.872	2.348
35	1.327 ₀	1.341 ₇	7.937	9.872	2.325
40	1.989	2.038	7.938	9.873	2.295
50	3.615	3.752	7.937	9.874	2.265
60	5.445	5.684	7.931	9.875	2.251
70	7.289	7.649	7.926	9.876	2.238
85	9.860	10.46 ₃	7.915	9.879	2.211
100	12.06 ₄	12.90 ₀	7.901	9.885	2.191
120	14.44	15.49	7.880	9.892	2.180
150	17.05	18.32	7.843	9.906	2.169
200	19.82	21.31	7.769	9.933	2.153
250	21.54	23.01	7.690	9.963	2.152
300	22.74	23.97	7.608	9.996	2.164

^aCalculated using α^{el} from Collins et al. (45).

^bBelow 22 K from Berg (73), above 22 K from Giauque and Meads (74), using the electronic term of Phillips (72).

^cKamm and Alers (77).

^dCalculated from $V_0 = 9.872 \text{ cm}^3/\text{mole}$ from Collins et al. (45) using integrated values^o ($\Delta L/L$) of the thermal expansion.

by Collins et al. (45), $V_0 = 9.872 \text{ cm}^3/\text{mole}$, again using integrated values of the thermal expansion. The lattice heat capacity was calculated from the smoothed results of Berg (73) below 20 K, and of Giauque and Meads (74) above 20 K, assuming the electronic contribution of Phillips (72), $C_p^{\text{el}} = aT$, $a = (1.35_0 \pm 0.01) \text{ mJ/mole} \cdot \text{K}^2$. A curve drawn through the plotted points has some small wiggles, a few percent in amplitude, which are probably due to the old (1941) heat capacity data of Giauque and Meads. The sharp bend in the plot just below 25 K reflects in part the marginal agreement between the heat capacity result of Berg (73) and of Giauque and Meads (74). The low temperature results of Collins et al. (45) also are plotted in Figure 20, and in their paper they also indicate a "corner" in $\gamma^{\text{lat}}(T)$ at about 25 K. Collins et al. quote three values of γ_0^{elas} , calculated from different data, which lie between 2.5 and 2.65. The low temperature rise in the Grüneisen parameter for aluminum is a little unusual for cubic metals. Collins et al. suggest that this is due to the fact that for many of the low-lying transverse lattice vibration modes the individual mode gammas [γ_i of Equation (1-14)] are significantly larger (2.5 - 2.8) than those for the longitudinal modes (2.3 - 2.4), i.e., the transverse modes are more sensitive to changes in volume than are the longitudinal modes in aluminum. However, there is no dramatic rise in γ^{lat} at low temperatures as some earlier measurements might suggest (38, 42, 48).

Conclusions

The present work gives the linear thermal expansion coefficient of copper from 5 K to 325 K and of aluminum from 10 K to 330 K. The accuracy of the smoothed results improves from $\pm 1\%$ at 10 K to $\pm 0.5\%$ near 20 K and to $\pm 0.1\%$ above 50 K, comparable to the scatter of the data. Good to excellent agreement exists with numerous previous results at higher temperatures; and the excellent overlap agreement with recent low temperature measurements (30, 31, 45) also supports the claimed quality of the present results. Copper and aluminum can now be used reliably as thermal expansion reference materials. Because they both have been measured in the same highly accurate apparatus, copper and aluminum now may serve also to evaluate another thermal expansion apparatus for systematic errors.

The "absolute" capacitance dilatometer which was used in conjunction with a highly sensitive capacitance bridge in the present work has proven to be an excellent yet relatively simple method to measure the linear thermal expansion coefficient of a cubic metal with high accuracy over a wide temperature range. The difficulties encountered below 10 K in the present work are believed to be due to the way in which the electrical leads to the sample were treated, and not inherent in the dilatometer design. It would be interesting to repeat the low temperature measurements to verify the theory that the physical arrangement of the electrical leads caused infinitesimal tipping of the sample which resulted in the erroneous low temperature thermal expansion data.

This shortcoming of the present work is not serious from an application standpoint, since White and Collins (31) and McLean et al. (30) for copper and Collins et al. (45) for aluminum provide the desired low temperature thermal expansion data.

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APPENDIX A. EXPERIMENTAL DATA

The following tables list the individual linear thermal expansion coefficient data points which were obtained in this experiment. The low temperature data points which were not used in the least-squares fitting (below 5.5 K for copper and 11 K for aluminum, see Chapter III) are given also.

Each data point is identified by a four digit point number. The first digit (0, 1, or 2) partitions the data into three segments. These segments correspond to the three distinct runs during which the copper data were taken (see Chapter III). The aluminum data were taken in one run, but conveniently partitioned for analysis. The second and third digits give the day of the month on which the point was taken, and the fourth digit identifies the order of points during the given day. Occasionally, two adjacent temperature intervals were combined into one point, for reasons as described in the main text, and these "combined intervals" are indicated in the tables by a point number of the form (abcd,e) meaning a combination of the intervals (abcd) and (abce).

The second and third columns of the tables give the temperature interval ΔT and the average temperature T_{avg} for the point. Temperatures below 30 K are based on a paramagnetic salt temperature scale T_x (64, 68), and above 35 K are based on the IPTS-68 scale (65, 66). Between 30 K and 35 K both scales were used; T_x dominates, but the scale differences do not significantly affect the results. The temperature interval ΔT is correct to the number of significant figures given, but

the average temperature may be in error by as much as 1 part in 10^5 (e.g., 3 mK at 300 K).

The fourth column gives the experimental linear thermal expansion coefficient data. The nominal accuracy of α is $\pm 0.1\%$ above 50 K, decreasing smoothly to $\pm 0.5\%$ near 20 K, and to $\pm 1\%$ at 10 K. Error limits on the unused low temperature data, estimated using Equation (III-6), are given following the thermal expansion coefficient. In general, one more digit is given for α than is justified by experimental accuracy. The data points are grouped according to the cell temperature which is given to the nearest degree in the last column of the tables. The temperature of the vacuum can was changed only occasionally and is indicated via footnotes to the tables.

Table A1. Thermal Expansion Data for Copper.

Point Number	ΔT (K)	T_{avg} (K)	α (K ⁻¹)	T_{cell}^* (K)
0011	5.109	312.503	16.878×10^{-6}	310 ^a
0012	5.321	317.718	16.931	
0021	5.009	323.135	16.981	
0041	5.056	72.489	7.374	69 ^b
0042	4.489	77.511	8.056	
0051	4.688	92.855	9.853	90
0052	4.686	98.042	10.363	
0053	4.658	103.214	10.834	
0054, 5	10.010	125.005	12.442	120
0056	4.539	147.789	13.605	145
0057	4.914	152.565	13.806	
0061	5.708	172.189	14.507	170
0062	5.018	177.552	14.661	
0063	5.032	199.213	15.228	197
0064	5.425	204.441	15.343	
0071	4.906	222.658	15.706	220
0072	4.906	227.564	15.793	
0073	4.946	247.710	16.108	245
0074	4.885	252.625	16.181	
0075	4.935	272.496	16.458	270
0076	5.095	277.511	16.505	

*Vacuum can temperature of 77 K (liquid nitrogen).

^a292 K (room temperature).

^b50 K (solid nitrogen).

Table A1. (Continued)

Point Number	ΔT (K)	T_{avg} (K)	α (K ⁻¹)	$T_{cell}^{\dagger}$ (K)
0201,2	1.989	11.258	4.224×10^{-8}	10
0211	1.569	15.716	11.929	15
0212	1.500	17.251	16.169	
0213	2.520	23.740	4.684×10^{-7}	22
0214	2.502	26.248	6.532	
0221	2.786	36.383	17.712	35
0222	2.227	38.888	21.192	
0223	5.074	47.465	3.449×10^{-6}	45
0224	5.001	52.499	4.271	
0231	4.998	62.502	5.893	60
0232	4.999	67.500	6.651	
0233	5.000	72.500	7.375	
0234	5.368	77.684	8.075	
1021,2	1.224	7.078	1.139×10^{-8}	6
1023	0.809	8.395	1.830	8
1024	0.900	9.250	2.399	
1031	0.998	10.001	3.011	10
1033	1.000	12.000	5.212	
1034	0.800	12.900	6.503	
1035	1.500	14.750	9.768	14
1036	1.499	16.250	13.337	
1037	1.500	17.749	17.774	
1038	1.123	19.011	22.46	
1039	1.477	20.261	27.54	

[†]Vacuum can temperature is 4.2 K (liquid helium) for all points.

Table A1 (Continued)

Point Number	ΔT (K)	T_{avg} (K)	α (K ⁻¹)	T_{cell} (K)
1041,2	0.548	2.226	8.73×10^{-10} ($\pm 13\%$)	2 ^c
1044	0.383	2.992	1.46×10^{-9} ($\pm 12\%$)	2.5 ^c
1046	0.400	3.800	2.431 ($\pm 7\%$)	3 ^c
1045-7 ^d	1.093	3.747	2.337 ($\pm 2\frac{1}{2}\%$)	
1051,2	1.000	4.500	3.564 ($\pm 2\%$)	4 ^c
105	1.000	5.000	4.664 ($\pm 1\frac{1}{2}\%$)	
1054	0.500	5.750	6.624	5.5 ^c
1054,5	1.000	6.000	7.292	
1055	0.500	6.250	8.023	
1062	0.454	6.227	8.199	5.5 ^e
1063,4	1.000	7.000	11.098	6.5 ^e
1064,5	1.000	7.500	13.273	
1072	0.551	8.775	2.073×10^{-8}	8 ^e
1073,4	0.949	9.275	2.631	
1076	1.000	10.500	3.463	10 ^e
1077	1.000	11.500	4.540	
1078	1.000	12.500	5.823	
1081	1.500	18.250	1.948×10^{-7}	17 ^e
1082	1.500	19.750	2.534	
1083	1.500	21.250	3.237	
1084	1.400	22.700	4.040	
1085	1.600	24.200	5.003	
1086	1.500	25.750	6.127	

^cVacuum can temperature of 1.4 K (pumped liquid helium).

^dCombination of three intervals.

^eVacuum can temperature of 4.2 K (liquid helium, 1 atm).

Table A1 (Continued)

Point Number	ΔT (K)	T_{avg} (K)	α (K ⁻¹)	$T_{\text{cell}}^{\dagger}$ (K)
1091	2.000	27.000	7.176×10^{-7}	26
1092	1.999	28.999	9.004	
1093	2.001	30.999	11.066	
1094	2.000	33.000	13.362	
1095	2.000	35.000	15.857	
1096	2.000	37.000	18.52	
1097	2.000	39.000	21.35	
1098	4.000	42.000	2.587×10^{-6}	40
1099	4.001	46.001	3.210	
1101	3.999	50.000	3.860	
1102	4.000	54.000	4.517	
1103	4.000	58.000	5.178	
1104	5.002	59.999	5.503	67
1105	5.000	65.000	6.279	
1106	5.000	70.000	7.011	
1107	5.000	75.000	7.720	
1108	5.000	80.000	8.371	
1111	5.000	95.000	10.070	92 ^f
1112	5.000	100.000	10.542	
1113	5.000	105.000	10.981	
1114	10.000	115.000	11.766	110 ^f
1115	10.000	125.000	12.423	

^f77 K (liquid nitrogen).

Table A1 (Continued)

Point Number	ΔT (K)	T_{avg} (K)	α (K ⁻¹)	T_{cell} (K)
2271	1.000	3.000	$1.466 \times 10^{-9} (\pm 1\frac{1}{2}\%)$	2.5 ^c
2273	1.000	4.000	2.611 ($\pm 1\frac{1}{2}\%$)	4 ^{c, g}
2292	1.000	9.000	2.198×10^{-8}	9 ^{e, g}
2293	1.000	10.000	3.001	
2294	1.000	11.000	3.980	
2295	1.000	12.000	5.140	
2296	1.000	13.000	6.603	
2297	1.000	14.000	8.206	
2021, 2	2.000	4.500	$3.540 \times 10^{-9} (\pm \frac{1}{2}\%)$	4 ^{c, g}
2022, 3	2.000	5.500	5.774 ($\pm \frac{1}{2}\%$)	
2031	1.000	13.000	6.586×10^{-8}	12 ^e
2032	1.000	14.000	8.234	
2033	1.000	1.500	10.28	

^gHeat switch closed for the sequence of points.

Table A2. Thermal expansion data for aluminum.

Point Number	ΔT (K)	T_{avg} (K)	α (K ⁻¹)	T_{cell}^* (K)
0101	5.000	87.500	10.330×10^{-6}	85
0102	5.000	92.500	11.092	
0103	4.968	97.484	11.827	
0111	5.000	117.500	14.284	115
0112	5.000	122.500	14.811	
0113	5.000	137.500	16.206	135
0114	5.000	142.500	16.617	
0121	10.027	149.987	17.190	
0122	10.000	160.000	17.881	
0123	10.000	170.000	18.504	
0124	15.000	192.500	19.669	183
0125	15.000	207.500	20.321	
0126	15.000	222.500	20.895	
0127	15.000	237.500	21.408	
0131	20.001	250.001	21.758	239
0132	19.995	269.999	22.321	
0133	20.004	289.998	22.815	
0141	5.593	302.794	23.081	292
0142	4.484	307.833	23.201	
0143	4.928	312.539	23.300	
0144	4.997	317.502	23.415	
0145	19.999	330.000	23.687	

*Vacuum can temperature is 77 K (liquid nitrogen) for all points.

Table A2. (Continued)

Point Number	$\Delta T^\dagger$ (K)	T_{avg} (K)	α (K ⁻¹)	$T_{\text{cell}}^{\dagger\dagger}$ (K)
1181	-2.000	34.000	12.459×10^{-7}	25
1182	-2.000	32.000	10.248	
1183	-2.000	30.000	8.3904	
1191	-2.000	26.000	5.2759	
1192	-2.000	24.000 ^a	4.0673	
1193	-1.800	22.100 ^a	3.1255	
1201	-2.004	20.002	23.050×10^{-8}	15
1202	-1.999	18.000	16.857	
1203	-2.001	16.000	12.103	
1204	-1.800	14.100 ^a	8.594	
1205	-2.000	14.000	8.522	11
1206	-2.000	12.000	5.723	
1207	-1.400	10.300 ^a	3.922	
1208	2.400	10.800 ^a	4.329	
1209	2.000	13.000	7.042	
1212	0.500	2.750	$4.10 \times 10^{-9} (+4\%)$	2.5 ^b
1213	0.230	3.115	4.61 (+7%)	
1214	-0.730	2.865	4.45 (+2%)	
1215	0.700	2.850	4.03 (+2½%)	
1216	0.500	3.250	4.76 (+3%)	3 ^b
1217	0.500	3.750	6.30 (+2½%)	
1216,7	1.000	3.500	5.51 (+1½%)	
1218	-1.000	3.500	5.89 (+1½%)	
1219	1.000	3.500	5.44 (+1½%)	

[†]Negative temperature interval when sample is cooled for the expansion coefficient measurement.

^{††}Vacuum can temperature of 4.2 K (liquid helium, 1 atm).

^aHeat switch closed for this point.

^bVacuum can temperature of 1.4 K (pumped liquid helium).

Table A2 (Continued)

Point Number	ΔT^+ (K)	T_{avg} (K)	α (K ⁻¹)	T_{cell}^{++} (K)
1221	0.500	4.250	$7.57 \times 10^{-9} (+2\%)$	4 ^b
1222,3	1.000	5.000	9.27 (+1%)	
1224	0.600	5.300	$1.079 \times 10^{-8} (+1\frac{1}{2}\%)$	5
1225	-0.600	5.300	1.100 (+1 $\frac{1}{2}$ %)	
1231	0.500	5.750	1.186 (+1%)	5.5
1232	0.500	6.250	1.404 (+1%)	
1233	-1.000	6.000	1.306 (+ $\frac{1}{2}$ %)	
1234	1.000	6.000	1.299 (+ $\frac{1}{2}$ %)	
1235	0.500	6.750	1.590 (+1%)	6.5
1236	0.500	7.250	1.853	
1237,8	0.700	7.850	2.225 (+ $\frac{1}{2}$ %)	
1251	0.999	6.500	1.492 (+ $\frac{1}{2}$ %)	6
1252	1.000	8.500	2.578 (+ $\frac{1}{2}$ %)	8
1253	1.000	9.500	3.323 (+ $\frac{1}{2}$ %)	
1254	0.600	10.300	4.026 (+ $\frac{1}{2}$ %)	
1255	1.000	10.500	4.187	10
1256	1.000	11.500	5.167	
1257	1.000	12.500	6.412	
1258	0.749	13.375	7.486	
2261	2.000	15.000	10.286	14
2262	2.007	17.004	14.412	
2263	2.006	20.997	2.674×10^{-7}	20
2264	2.033	23.016	3.552	
2265	1.966	25.016	4.625	

Table A2 (Continued)

Point Number	ΔT (K)	T_{avg} (K)	α (K ⁻¹)	T_{cell}^{++} (K)
2266	1.999	31.001	9.272×10^{-7}	30
2267	2.000	33.001	11.318	
2268	2.000	35.000	13.615	
2269	3.015	37.507	16.781	
2270	2.985	40.507	20.987	
2271	3.886	47.025	3.147×10^{-6}	45
2272	4.377	51.152	3.866	
2273	3.665	55.168	4.602	
2274	5.000	59.500	5.410	
2275	4.000	64.000	6.249	
2276	3.999	68.000	6.989	
2281	4.005	71.004	7.537	
2282	4.182	75.098	8.262	
2283	3.813	79.094	8.947	
2284	4.080	83.041	9.611	
2285	4.719	87.441	10.313	68
2286	5.000	92.300	11.059	
2287	5.215	97.408	11.795	
2288	4.985	102.507	12.488	
2321	14.568	298.150	22.960	
2322	9.839	310.353	23.260	

^cVacuum can temperature of 230 K, coupled by exchange gas, to 77 K (liquid nitrogen) in outer dewar.

APPENDIX B. FINITE TEMPERATURE INTERVAL CORRECTION

The linear thermal expansion coefficient was defined in Chapter I as

$$\alpha = \frac{1}{L} \left(\frac{\partial L}{\partial T} \right)_P ; \quad (B-1)$$

but experimentally a finite length change due to a finite temperature interval is measured, and the linear thermal expansion coefficient is approximated as

$$\bar{\alpha} = \frac{1}{L} \left(\frac{\Delta L}{\Delta T} \right)_P . \quad (B-2)$$

This approximation is satisfactory for work requiring an accuracy of one percent or so. However, when the temperature interval ΔT is of the order of $T/10$, the difference between $\bar{\alpha}$ and α approaches one percent when the thermal expansion coefficient varies rapidly with temperature. For precision work with a desired accuracy of $\pm 0.1\%$, a correction must be made for this finite temperature interval error.

Integrating Equation (B-1) leads to

$$L(T) = L(0) \exp \left[\int_0^T \alpha(T) dT \right] , \quad (B-3)$$

where $L(T)$ is the length of the sample at temperature T . Consider a thermal expansion measurement with a temperature interval ΔT about the average temperature T_0 for which Equation (B-2) is written as

$$\bar{\alpha}(T_0) = \frac{L(T_0 + \Delta T/2) - L(T_0 - \Delta T/2)}{L(T_0) \Delta T} . \quad (B-4)$$

Now

$$\begin{aligned}
 L(T_0 \pm \Delta T/2) &= L(0) \exp \left[\int_0^{T_0 \pm \Delta T/2} \alpha(T) dT \right] \\
 &= L(0) \exp \left[\int_0^{T_0} \alpha(T) dT \right] \exp \left[\int_{T_0}^{T_0 \pm \Delta T/2} \alpha(T) dT \right] \\
 &= L(T_0) \exp \left[\int_{T_0}^{T_0 \pm \Delta T/2} \alpha(T) dT \right] \\
 &\approx L(T_0) \left[1 + \int_{T_0}^{T_0 \pm \Delta T/2} \alpha(T) dT \right], \quad (B-5)
 \end{aligned}$$

so that a substitution of Equation (B-5) into Equation (B-4) results in

$$\begin{aligned}
 \bar{\alpha}(T_0) &\approx \frac{1}{\Delta T} \left[\int_{T_0}^{T_0 + \Delta T/2} \alpha(T) dT - \int_{T_0}^{T_0 - \Delta T/2} \alpha(T) dT \right] \\
 &\approx \frac{1}{\Delta T} \left[\int_{T_0 - \Delta T/2}^{T_0 + \Delta T/2} \alpha(T) dT \right]. \quad (B-6)
 \end{aligned}$$

Next expand $\alpha(T)$ in a Taylor's series about T_0 :

$$\alpha(T) = \sum_{n=0}^{\infty} \frac{1}{n!} \alpha^{(n)}(T_0) (T - T_0)^n, \quad (B-7)$$

where $\alpha^{(n)}(T_0)$ is $(\partial^n \alpha / \partial T^n)$ evaluated at T_0 . Substitute this into the

integral of Equation (B-6)

$$\begin{aligned}
 \bar{\alpha}(T_o) &= \frac{1}{\Delta T} \left[\int_{T_o - \Delta T/2}^{T_o + \Delta T/2} dT \sum_{n=0}^{\infty} \frac{1}{n!} \alpha^{(n)}(T_o) (T - T_o)^n \right] \\
 &= \sum_{n=0}^{\infty} \frac{1}{n!} \alpha^{(n)}(T_o) \frac{1}{\Delta T} \left[\int_{T_o - \Delta T/2}^{T_o + \Delta T/2} (T - T_o)^n dT \right] \\
 &= \sum_{n=0}^{\infty} \frac{1}{n!} \alpha^{(n)}(T_o) \frac{1}{\Delta T} \frac{1}{(n+1)} \left[\left(\frac{\Delta T}{2} \right)^{n+1} - \left(-\frac{\Delta T}{2} \right)^{n+1} \right].
 \end{aligned}$$

The term in the brackets is zero for odd values of n , and is $2(\Delta T/2)^{n+1}$ for n even. Thus

$$\bar{\alpha}(T_o) = \sum_{\substack{n=0 \\ \text{even}}}^{\infty} \frac{1}{(n+1)!} \alpha^{(n)}(T_o) \left(\frac{\Delta T}{2} \right)^n. \quad (B-8)$$

The $n = 0$ term in Equation (B-8) is just $\alpha(T_o)$ which may be moved to the other side of the equality to give the finite temperature interval error:

$$\begin{aligned}
 \bar{\alpha}(T_o) - \alpha(T_o) &= \sum_{\substack{n=0 \\ \text{even}}}^{\infty} \frac{1}{(n+1)!} \alpha^{(n)}(T_o) \left(\frac{\Delta T}{2} \right)^n \\
 &= \frac{1}{24} \alpha''(T_o) (\Delta T)^2 + \frac{1}{1920} \alpha^{(iv)}(T_o) (\Delta T)^4 + \dots
 \end{aligned} \quad (B-9)$$

The second derivative is usually more than sufficient to estimate the

correction to be applied to the experimental $\bar{\alpha}$ to obtain the true linear thermal expansion coefficient α . The second derivative can be calculated from a rough fit to the experimental data.