

# Method for extrapolating the compressibility data of solids from room to lower temperatures

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Around room temperature, the elastic constants of solids can be measured comfortably applying commercial equipment, e.g. resonant ultrasound spectroscopy (RUS) devices, whereas at low temperatures special efforts are necessary. To decrease the effort, a method has been developed and tested for extrapolating data on the compressibility of solids to lower temperatures. The method is based on well-known approximate relations between the thermodynamic properties of solids, the derivation of which was pioneered by Grüneisen and the measurement of quantities, which are easier accessible experimentally than the elastic constants (thermal expansion, specific heat). In essence, the extrapolation uses data on the

thermal expansion. The applicability of the method has been tested for copper, the properties of which are documented comprehensively in literature even at low temperatures. In a second step, the method has been applied to extrapolate the compressibility data of a copper beryllium-cobalt alloy from near room temperature down to about 80 K with a relative uncertainty of order 0.1%. This extrapolation is needed for and verified by dielectric-constant gas thermometry, a special kind of primary thermometry for determining thermodynamic temperatures. For such gas thermometry experiments cylindrical capacitors, the electrodes of which have been made from the investigated copper beryllium alloys, are used.

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**1 Introduction** The original goal of this work is to achieve independent information on the total pressure distortion of two cryo-capacitors, expressed as an effective compressibility  $\kappa_{\text{eff}}$ , in dependence on temperature. The cryo-capacitors are used at PTB as sensors for performing dielectric-constant gas thermometry (DCGT) [1], a special kind of primary thermometry for determining thermodynamic temperatures.  $\kappa_{\text{eff}}$  is dominated by the compressibility of the capacitor electrodes, i.e., an elastic property of solids.

Around room temperature, the elastic constants of solids can be measured comfortably applying commercial equipment, e.g., resonant ultrasound spectroscopy (RUS) devices, whereas at low temperatures below the application range of liquid-bath thermostats special efforts are necessary. To decrease the effort, a method has been developed and tested for extrapolating data on the compressibility of solids to lower temperatures. The method is also useful for other experiments, which require to know the temperature dependence of the compressibility of construction materials.

This is for example the refractive index gas-thermometry, a method with which a growing community is performing thermodynamic temperature measurements.

The article is organized as follows: the theoretical background and the method used to derive the temperature dependence are described in the next section. In the third section, the method is tested applying the comprehensive literature data for pure copper, which gives an estimate for the achievable extrapolation uncertainty. The fourth section deals with the measurement of different properties of the CuBeCo capacitor materials (specific heat, thermal expansion, compressibility near room temperature). Finally, individual temperature dependences for the two cryo-capacitors are presented together with uncertainty estimates as basis for DCGT measurements at low temperatures. The uncertainty estimates are checked by comparing the DCGT results with those obtained with other kinds of primary-thermometry methods, especially acoustic gas thermometry.

## 2 Theoretical background

**2.1 Thermodynamic relations** In this article, the treatment of the temperature dependence of the bulk compressibility  $\kappa = \partial \ln V / \partial p$  ( $p$  pressure,  $\kappa = -1/B$ ,  $B$  bulk modulus) is based on the following relation between the temperature dependence of  $\kappa$  and that of the volume  $V$ :

$$\frac{\partial \ln \kappa_S / \partial T}{\partial \ln V / \partial T} = \delta, \quad (1)$$

where  $\kappa_S$  is the adiabatic compressibility,  $T$  is the thermodynamic temperature, and  $\delta$  is the Anderson–Grüneisen parameter. Equation (1) has been first derived by Grüneisen [2] and somewhat generalized by Anderson [3] (Lawson and Ledbetter [4] also dealt with this relation, but they introduced *ad hoc* equations without a fundamental derivation). Equation (1) is equivalent to

$$\frac{\kappa_S(T)}{\kappa_S(T_0)} = \left( \frac{V(T)}{V(T_0)} \right)^\delta, \quad (2)$$

where  $T_0$  is a reference temperature.

A simple relation between the temperature dependencies of  $\kappa$  and  $V$  is surprising because both the elastic constants and the thermal expansion are connected with anharmonic effects in solids, which are complicated phenomena, see for instance Ref. [5]. A simple atomistic theory of anharmonic effects does not exist. To assess the relevance of Eq. (1) it is, therefore, important to look at Grüneisen's derivation, and especially at his assumptions.

Grüneisen started with the general Virialsatz of a solid [6] and assumed the Mie potential [7]

$$\Phi = -\frac{A}{V^m} + \frac{B}{V^n}, \quad (3)$$

in which  $A$ ,  $B$ ,  $m$ , and  $n$  are constants. (Anderson [3] derived Eq. (1) for a more general potential.) The first term of  $\Phi$  describes attraction, and the second one repulsion. This allowed him to derive the Mie–Grüneisen equation of state relating pressure and volume.

$$pV + V \frac{d\Phi}{dV} = \gamma E, \quad (4)$$

where  $\gamma$  is the Grüneisen parameter and  $E$  is the thermal energy. To proceed further, he made the following important assumptions, cf. Ref. [3]:

- (i) The vibrational energy of the atoms is equal to the thermal energy.
- (ii) Quasi-harmonic approximation with only one vibrational frequency  $\nu$ , which is independent of temperature. (Anderson [3] applied the Debye model [8].)
- (iii) Existence of only one temperature-independent Grüneisen parameter.

- (iv) The relative adiabatic pressure dependencies of vibrational frequency and temperature are equal.
- (v) The volume at high temperature differs little from that at absolute zero.
- (vi) The pressure  $p$  is small compared to the bulk modulus  $B$ .

With these assumptions, Grüneisen obtained simple relations for the Grüneisen parameter  $\gamma$  and the Anderson–Grüneisen parameter  $\delta$

$$\gamma = \frac{\alpha_V}{\kappa_S c_p \rho}, \quad (5)$$

$$\delta = m + n - \gamma + 2, \quad (6)$$

where  $\alpha_V$  is the coefficient of volume thermal expansion,  $c_p$  is the specific heat capacity at constant pressure, and  $\rho$  is the density.

Grüneisen's assumptions represent very strong simplifications. For instance, the Grüneisen parameter is defined as  $\gamma = -\partial \ln \nu / \partial \ln V$  (in the Debye model, the definition is  $\gamma = -\partial \ln \Theta / \partial \ln V$  with  $\Theta$  being the Debye temperature).  $\gamma$  is different for the various vibrational modes, and its value is usually much larger for longitudinal modes than for transversal ones. In view of the complexity of the phenomena, it is not possible to estimate generally the uncertainty, which is connected with the application of Eq. (1) together with Eqs. (5) and (6). Therefore, another way combining different checks was chosen to get an uncertainty estimate for the extrapolation method described below. First, the method was applied to copper, see Section 3. The properties of copper are near to those of the electrode material and there exist reliable experimental data for all needed thermophysical properties of copper. Second, the results obtained for the electrode material with the extrapolation method were compared with values deduced from the compressibility data of copper using the ratio  $\kappa_{CuBeCo} / \kappa_{Cu}$  at the triple point of water (TPW) as scaling factor, see Section 5. Third, the uncertainty propagation applying Eqs. (1), (5), and (6) was estimated by performing Monte-Carlo simulations.

**2.2 Extrapolation method** For determining the compressibility of the measuring capacitors at low temperatures, the following extrapolation method has been established. Starting point is the measurement of DCGT isotherms (pressure versus dielectric constant at constant temperature) at the TPW [1], the evaluation of which yields an *in situ* determination of the isothermal effective compressibility  $\kappa_{\text{eff}}(273.16 \text{ K})$  of the capacitor since the thermodynamic temperature of the TPW is known by definition. The rigid capacitor is a complicated geometrical object because electrically isolating pieces and stabilizing screws are necessary. Thus, an *in situ* determination is of crucial importance for correction purposes. The second step is the measurement of the thermophysical quantities contained in Eqs. (1) and (5) in a temperature range around

the TPW as described in detail below. (The temperature range is confined by the technique applied for determining the adiabatic bulk compressibility of the electrode material.) The selected value of the parameter  $\delta$  to be used for the extrapolation to lower temperatures is the mean value in a range of a few 10K including the TPW. For the extrapolation, in principle Eq. (2) is applied with  $T_0 = 273.16$  K and  $\kappa_S(273.16$  K) as reference values. In the present work, the linear thermal expansion of the capacitor electrodes is obtained from the temperature dependence  $C(T)$  of the capacitance of the cylindrical capacitor, i.e., the working equation for the extrapolation of the adiabatic bulk compressibility is

$$\kappa_S(T) = \kappa_S(273.16 \text{ K}) \left( \frac{C(T)}{C(273.16 \text{ K})} \right)^{3\delta}, \quad (7)$$

where the factor three in the exponent considers that the linear thermal expansion coefficient is one third of the volume one ( $\alpha_V = 3\alpha_L$ ). For DCGT, the isothermal compressibility  $\kappa_T$  is relevant. The relation between  $\kappa_T$  and  $\kappa_S$  is a fundamental thermodynamic relation also given in [2]

$$\kappa_T(T) = \kappa_S(T)(1 + \gamma T \alpha_V), \quad (8)$$

which leads together with Eq. (7) to

$$\kappa_T(T) = \kappa_S(273.16 \text{ K}) \left( \frac{C(T)}{C(273.16 \text{ K})} \right)^{3\delta} (1 + \gamma T \alpha_V), \quad (9)$$

and with reference to  $\kappa_{\text{eff}}(273.16$  K) determined at the TPW (application of the scaling factor  $\kappa_{\text{eff}}(273.16$  K)/ $\kappa_S(273.16$  K)) to

$$\kappa_{\text{eff}}(T) = \kappa_{\text{eff}}(273.16 \text{ K}) \left( \frac{C(T)}{C(273.16 \text{ K})} \right)^{3\delta} (1 + \gamma T \alpha_V). \quad (10)$$

The correction factor  $(1 + \gamma T \alpha_V)$  requires to investigate the thermal expansion of the capacitor material  $\alpha_V \approx 3\partial \ln C(T)/\partial T$  in the whole temperature range of interest. Since Eq. (10) is a non-linear one, the uncertainty propagation from the different input quantities can be estimated only by performing Monte-Carlo simulations.

In the extrapolation method described above, only the determination of the starting value ( $\kappa_{\text{eff}}(273.16$  K)) and the measurement of the thermal expansion via the temperature dependence  $C(T)$  are special solutions for the DCGT measuring capacitors. Thus, it can be adapted for other experiments, which require to know the temperature dependence of the compressibility of construction materials, see the next section.

### 3 Application to copper and other materials

Pure copper is surely one of the best examined materials. The quantities, relevant for the method described in the

preceding section have all been well investigated even at lowest temperatures. The compressibility of mono-crystalline copper was studied extensively by Overtone and Gaffney [9], and that of poly-crystalline copper by Ledbetter [10]. The thermal expansion of copper and a copper beryllium alloy was determined very carefully by Holtz and Swenson [11]. For the specific heat capacity at constant pressure, data are summarized by White and Collocott [12] with claimed uncertainties on the percent level. Using this input data together with Eq. (1) and (5), it is possible to calculate the Grüneisen parameter  $\gamma_{\text{copper}}$  and the Anderson-Grüneisen parameter  $\delta_{\text{copper}}$  and check their independence of temperature. The results are shown in Fig. 1 in the range from below 50 K to 300 K. The strong increase of  $\delta_{\text{copper}}$ , deduced applying Eq. (1), is compatible with the uncertainty of the compressibility because at low temperatures,  $\kappa_S$  becomes nearly independent of temperature. But in the range above about 80 K, being of interest in this article, the two parameters are constant at a surprising level.

For applying the extrapolation method to copper, the following adaption of Eq. (9) has been used:

$$\kappa_T(T) = \kappa_S(T_0)(1 + \alpha_L(T - T_0))^{3\delta} (1 + \gamma T \alpha_V), \quad (11)$$

where  $\alpha_L$  is the coefficient of linear thermal expansion. The results obtained for  $T_0 = 273.16$  K are shown in Fig. 2, in which the relative deviation between the extrapolated and the experimental values is drawn versus temperature both for the adiabatic and the isothermal compressibility. Down to 80 K, the deviation is well below 0.1%. This level of coincidence is by far sufficient for achieving the necessary small uncertainty of DCGT, see Section 5.

Copper has a well-known regular behavior. It is suspected that the developed extrapolation method is applicable in the temperature range at least down to liquid-nitrogen temperatures for all materials having a regular behavior. Criteria for assessing the behavior are

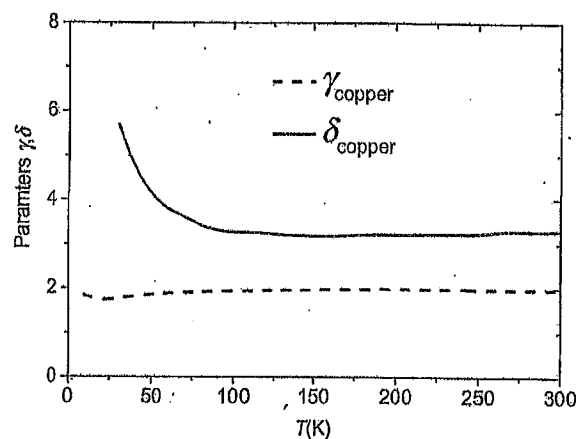
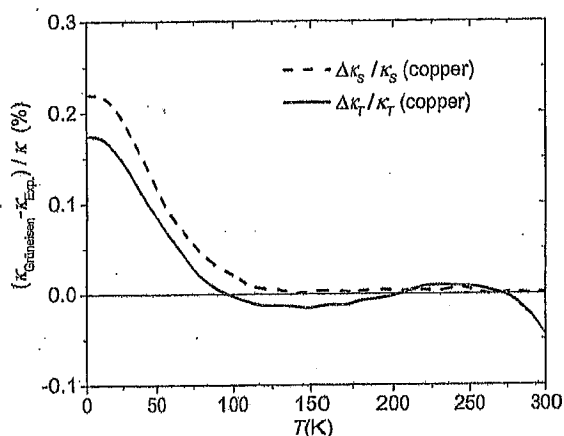


Figure 1 Grüneisen parameter  $\gamma_{\text{copper}}$  and Anderson-Grüneisen parameter  $\delta_{\text{copper}}$  of copper versus temperature.



**Figure 2** Relative deviation between extrapolated  $\kappa_{\text{Grüneisen}}$  and experimental values  $\kappa_{\text{exp}}$  of the adiabatic and isothermal compressibility, respectively, of copper versus temperature.

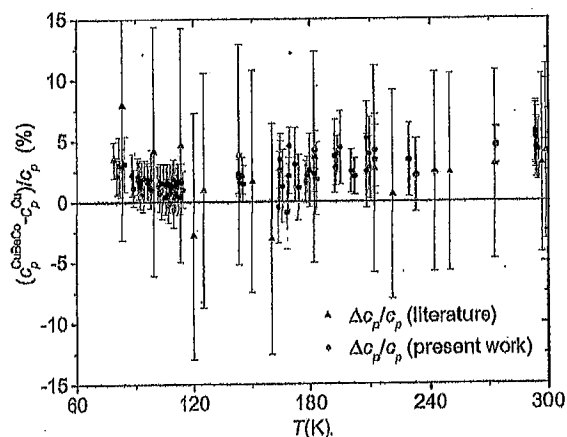
given in Refs. [4, 13]. One criterion is for instance the relationship between experimental data for the Anderson-Grüneisen parameter and the Grüneisen parameter. Metals, the parameters of which correspond to the relationship found in Ref. [4] within 20%, can be considered as regularly. The criteria given in Ref. [13] concern permitted values of the parameters of the Mie-Lennard-Jones potential as well as correlations between the atomic mass and the Grüneisen parameter, the Debye temperature, and the coordinate of the minimum of the potential, respectively.

**4 Measurement of material properties** In contrast to copper, the copper beryllium alloys are not so well known though many properties of different alloys are summarized in a monograph [14]. The partially large uncertainties and the differences in composition, heat treatment etc. made measurements of different thermo-physical quantities necessary for obtaining input data near room temperature. In the present case, the material of the capacitor electrodes is the alloy C17500 with a nominal content of (0.4–0.7)% beryllium and (2.4–2.7)% cobalt in copper. Performing careful mass and dimensional measurements, a mean density of  $8749(20) \text{ kg m}^{-3}$  was determined for four C17500 samples at  $20^\circ\text{C}$ . A comparison with the density of pure copper does not allow to get an estimate of the cobalt content, because the density of cobalt and copper is very close, but the beryllium content could be estimated to be about 0.5%.

**4.1 Specific heat capacity** In an especially designed vacuum chamber surrounded by a thermal bath, a cylinder made of C17500 was measured. The cylinder was made from the same batch as the capacitor, which was used in the latest DCGT measurements. The chamber can be temperature stabilized between 77 K and room temperature, whereby the most stable temperatures are achieved at 77 K with liquid nitrogen and at 273 K with an ice water mixture.

The measurements were performed by a heat-pulse method. The limiting factors in uncertainty were not the temperature, power, and mass measurements (all below the tenth of a percent level), but the stability in the thermal conditions (changing heat fluxes etc.). Therefore, several measurements at various temperatures with completely different thermal conditions of the surroundings were performed leading to uncertainties between 1.5% and 3%. The results obtained for the specific heat  $c_p$  and their uncertainty estimates are shown in Fig. 3 as relative deviation from  $c_p$  of copper. For comparison, data of a slightly different alloy from Ref. [14] is shown in the same representation. It is clearly visible that the specific heat capacity of C17500 is larger than that of pure copper. This is related to the larger heat capacity of both beryllium and cobalt. But in general, the temperature dependence of the alloy agrees on the level of a few percent with that of pure copper.

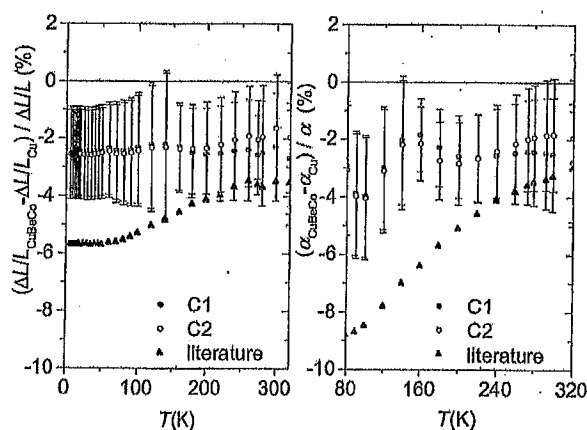
**4.2 Thermal expansion** The linear thermal expansion can be determined *in situ* by a capacitance measurement. In the cylindrical geometry, only the length change of the electrode results in a capacitance change. The change of the radii cancels out. This is true for the thermal expansion as well as for the deformation under pressure. For the capacitance measurement, an absolute capacitance bridge (Andeen Hagerling AH 2500A with option E) with a resolution of 0.07 ppm and a long-term drift of 0.5 ppm per year was used. In this case, the uncertainty of the thermal expansion is not dominated by the capacitance measurement but by the temperature inhomogeneity caused by partly large temperature sweep rates. For two cylindrical capacitors identified as C1 and C2, the measurements were taken out between 2 and 300 K over a period of 2 weeks. This leads to a spread of capacitance data on the 10 ppm level resulting in relative uncertainties of the changes on the percent level. The relative length change  $\Delta L/L$ , which has



**Figure 3** Relative deviation between the specific heat of copper-beryllium-cobalt alloys and copper versus temperature: filled dots – present work; triangles – literature data [14]. The uncertainty bars correspond to the standard uncertainty.

been deduced in good approximation from the relative capacitance change, is shown on the left side of Fig. 4 as relative deviation from that of pure copper. It is visible that in the whole temperature range, the temperature dependence of the thermal expansion of the capacitor material C17500 follows the behavior of pure copper with an offset of about 2%. Compared to the literature data of [11], there is an offset due to the smaller content of beryllium, which has the lowest thermal expansion of the three components (copper, cobalt, and beryllium). On the right side of Fig. 4, the relative deviation between the thermal expansion coefficients  $\alpha$  of CuBeCo and copper is shown. The information is equivalent to the left side, but the temperature range is smaller because the  $\alpha_{C17500}$  was extracted from the derivative of a simple polynomial fit to the capacitance data. Below 80 K, the slope of the temperature dependence of the thermal expansion decreases rapidly, and this results in an increased scatter of the  $\alpha_{C17500}$  values. The left side of the figure makes clear that this is simply a mathematical and not a physical issue. In summary, it is clear that the capacitors as composite objects behave very similar to pure copper.

**4.3 Adiabatic bulk modulus** The adiabatic bulk modulus  $B_S$  has been determined by resonant ultrasound spectroscopy (RUS), a method widely applied in non-destructive testing [15, 16]. Only specimen's normal-mode frequencies of free vibration were used along with the shape and mass to determine its elastic properties. Measurements were performed in the range from 230 to 330 K on three parallelepipeds and a cylinder as specimens. They were cut from the same rod of C17500 material, from which the

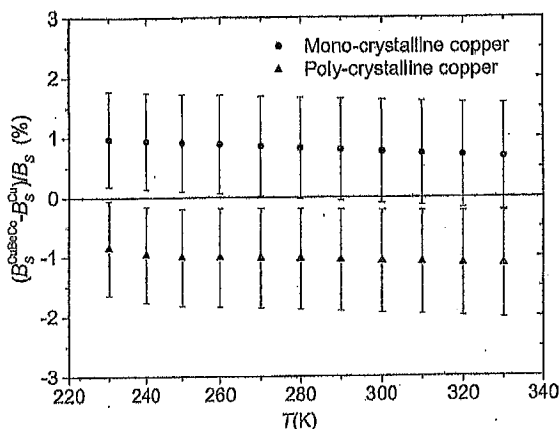


**Figure 4** On the left: Relative length change  $\Delta L/L_{\text{CuBeCo}}$  of CuBeCo alloys with reference to 293 K versus temperature.  $\Delta L/L_{\text{CuBeCo}}$  is shown as relative deviation from  $\Delta L/L_{\text{Cu}}$  of copper. The symbols represent the following data: filled dots – capacitor C1; unfilled dots – capacitor C2; triangles – literature data [11]. The uncertainty bars correspond to the standard uncertainty. On the right: Relative deviation between the coefficients of linear thermal expansion of the CuBeCo alloys and that of copper.

capacitor electrodes were manufactured. The comparison of the results obtained for samples, which are different with respect to their dimensions and geometry, allowed to estimate how representative they are for the material comprising the capacitor electrodes.

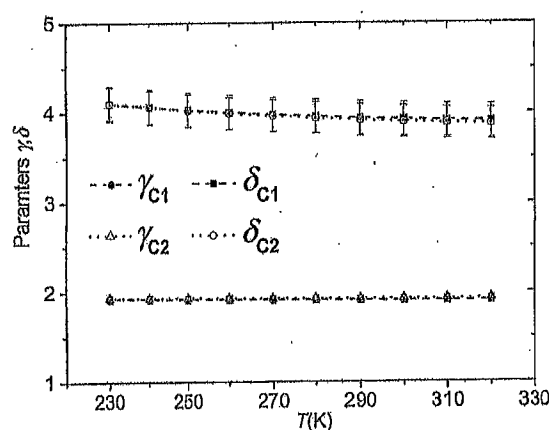
In the fit routine described in Refs. [15, 16], for polycrystals mostly the isotropic case (two free parameters) is used to describe the resonance frequencies. This model works perfectly for tungsten carbide samples [17]. A well known problem of hardened copper beryllium is an increased grain size, leading to certain anisotropy. To account for this effect, it is necessary to consider a possible lower microscopic crystal symmetry. For this reason, the resonance frequencies have been fitted with a different number of free fit parameters (the number increases with decreasing symmetry), and the fit residuals have been evaluated as an indicator of the fit quality. It was clearly visible that for all specimens, the isotropic evaluation had too large fit residuals, and the isotropic results deviated significantly from the expected value estimated from elastic-constant data published in Ref. [14]. However, if the evaluation is performed for cubic symmetry (three free parameters), tetragonal symmetry (six free parameters), or orthogonal symmetry (nine free parameters), the fit residuals are much smaller. The use of more fit parameters for lower symmetry is not a generally applicable method, but in the case discussed here, such a consistency check can be performed. Namely, the resulting bulk modulus and the other elastic constants are consistent with literature data and, moreover, show very good agreement with an independent determination via DCGT (see next section) within the uncertainty estimates. To account for a certain model ambiguity, the final result is a weighted mean of the results obtained for the different samples and evaluated with three, six, and nine free parameters. The uncertainty has been estimated by applying a rectangular distribution on the interval between the maximum and minimum values. All other uncertainty components arising from mass, dimensional, and frequency measurements are much smaller. The final relative uncertainty due to the influence of anisotropy of about 0.8% is a factor of eight larger than the uncertainties achieved with other capacitor materials like tungsten carbide in Ref. [17], but is still sufficiently small to extract the Anderson–Grüneisen parameter for which mainly the temperature dependence of  $\kappa$  is relevant (see Eq. (1)). The obtained final data for the adiabatic bulk modulus of the alloy C17500 is compared with literature data [9, 10] for mono- and polycrystalline copper, respectively, in Fig. 5.

Using the results for alloy C17500 illustrated in Fig. 5 together with the heat capacity and thermal expansion data determined as described in Section 4.1 and 4.2, the Grüneisen parameter  $\gamma$  and the Anderson–Grüneisen parameter  $\delta$  have been calculated in the temperature range from 230 to 320 K. The obtained temperature dependencies are shown in Fig. 6. The data for both capacitors yield a perfect independence of temperature for  $\gamma$ . The change of  $\delta$  is compatible with the standard uncertainty estimates.



**Figure 5** Relative deviation between the adiabatic bulk modulus of the CuBeCo alloy C17500 and mono- and polycrystalline copper, respectively, versus temperature: dots – monocrystalline copper [9]; triangles – polycrystalline copper [10]. The uncertainty bars correspond to the standard uncertainty.

**4.4 Isothermal compressibility at the TPW** To come as close as possible to the properties of the two measuring capacitors C1 and C2, respectively, the isothermal compressibility was determined *in situ* with DCGT. As described in detail in Ref. [1], several isotherm measurements with helium were made for each capacitor at the TPW, which has the defined thermodynamic temperature of 273.16 K. Applying the *ab initio* calculation of the polarizability of helium [18], the compressibility can be determined from the slope of the isotherms at low pressure describing the ideal-gas behavior. For capacitor C1 an



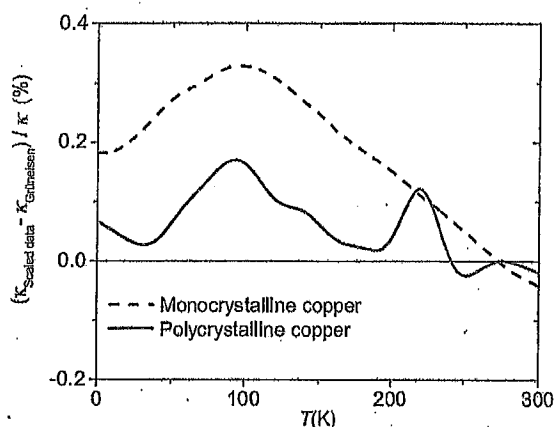
**Figure 6** Grüneisen parameter  $\gamma$  and Anderson–Grüneisen parameter  $\delta$  of CuBeCo alloy C17500 deduced from the data obtained with the two measuring capacitors C1 and C2, respectively, versus temperature. The symbols represent the following values: Filled circles and squares represent  $\gamma$  and  $\delta$  of C1, respectively, unfilled triangles and circles represent  $\gamma$  and  $\delta$  of C2.

effective compressibility of  $\kappa_{\text{eff}}^{\text{C1}}(273.16\text{K}) = -2.485(7) \times 10^{-12} \text{Pa}^{-1}$  has been determined, and for capacitor C2 a value of  $\kappa_{\text{eff}}^{\text{C2}}(273.16\text{K}) = -2.466(10) \times 10^{-12} \text{Pa}^{-1}$ . The term “effective” indicates the fact that each capacitor is a composite because small pieces of insulator materials are necessary to isolate the electrodes electrically. In addition different electrode or shield materials can lead to stronger deviations from the expected length compressibility for the cylindrical symmetry.

The adiabatic bulk compressibility of the electrode material  $\kappa_{\text{S}}^{\text{RUS}}(273.16\text{K}) = -7.20(6) \times 10^{-12} \text{Pa}^{-1}$ , determined by RUS as discussed in the former section, can be transferred to the isothermal length compressibility  $\kappa_{\text{T}}^{\text{RUS}}(273.16\text{K})/3 = -2.46(2) \times 10^{-12} \text{Pa}^{-1}$ . A comparison of the RUS and the DCGT value shows a perfect agreement well inside the combined uncertainty estimates of both. This is a clear indication that the procedure used for the determination of the elastic constants via RUS is reliable. Details concerning the isotherm data and their evaluation including the estimation of the uncertainty will be published in Ref. [19].

**5 Results for CuBeCo alloy C17500** Using  $\kappa_{\text{eff}}^{\text{C1}}(273.16\text{K})$  and  $\kappa_{\text{eff}}^{\text{C2}}(273.16\text{K})$  as starting values, respectively, the effective compressibilities of the two measuring capacitors down to 80 K have been determined by extrapolation applying the method described in Section 2.2. The thermophysical quantities contained in Eq. (1) and (5) have been measured in the temperature range from 230 to 323 K as discussed in Section 4. The selected value of the parameter  $\delta$  to be used for the extrapolation to lower temperatures is the mean value in the reduced range from 270 to 323 K. The data below 270 K allow to perform additional checks, see Fig. 6. The relative standard deviation of the individual  $\delta$  values from the mean value is smaller than 1%. For evaluating the quality of the extrapolation, the following checks and uncertainty estimations have been performed: comparison with data for copper to deduce the uncertainty of the model; Monte-Carlo simulations to get an information on the influence of the uncertainty of the input thermophysical quantities; comparison of DCGT results near 80 K with those obtained with other primary thermometry methods.

**5.1 Comparison with copper** Since the alloy C17500 contains only about 3% alloying elements, it can be expected that the behaviors of the alloy and copper are very similar. An interesting check is, therefore, to scale the temperature dependence of the compressibility of copper  $\kappa_{\text{Cu}}(T)$  with the factor  $S = \kappa_{\text{eff}}(273.16\text{K})/\kappa_{\text{Cu}}(273.16\text{K})$  and to compare the scaled values  $\kappa_{\text{Scaled data}}(T) = S \kappa_{\text{Cu}}(T)$  with the extrapolation results  $\kappa_{\text{Grüneisen}}$ . This is done in Fig. 7 for the material of capacitor C1 and data for mono- and polycrystalline copper, respectively, taken from Refs. [9, 10]. (The oscillations of the curve for polycrystalline copper are caused by the literature data.) The maximum relative

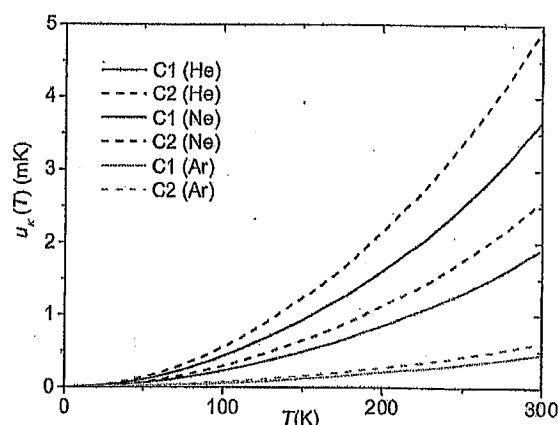


**Figure 7** Temperature dependence of the relative deviation between scaled copper data for the isotherm compressibility  $\kappa_{\text{Scaled data}}$ , see text, and the extrapolated compressibility  $\kappa_{\text{Grüneisen}}$  of the CuBeCo alloy C17500 as represented by the results for capacitor C1; dashed line – monocrystalline copper [9]; full line – polycrystalline copper [10].

deviation around 100 K is smaller than 0.35%, which corresponds to a relative standard uncertainty of only 0.1% applying a rectangular probability distribution. In view of the excellent extrapolation results for copper presented in Section 3, a model uncertainty of 0.1% at 80 K seems to be very conservative.

**5.2 Monte-Carlo simulations** In order to achieve uncertainty estimates for the extrapolated compressibilities, derived with Eq. (10), a Monte-Carlo simulation was performed. Here the input quantities, namely  $\rho$ ,  $c_p(T)$ ,  $\Delta L(T)/L(T)$ ,  $\alpha_L(T)$ ,  $B(T)$ , and  $\kappa_{\text{eff}}(273.16 \text{ K})$ , are varied by the use of random normally distributed numbers, where the variation was performed on the level of the uncertainty estimated for the specific quantity (shown in the specific figures in Section 4). The clearly dominating uncertainty component is  $u(\kappa_{\text{eff}}(273.16 \text{ K}))$ . The determination of  $\kappa_{\text{eff}}(273.16 \text{ K})$ , cf. Section 4.4, is based on low density isotherms (pressure up to 0.3 MPa) [19] and, therefore, the uncertainty is at least about a factor of three larger than in Ref. [17], where the maximum pressure was 7 MPa. The other uncertainty components are an order of magnitude smaller. They cause a relative uncertainty of the extrapolation at 80 K of only 0.1%. Thus, the simulations make clear that there is still a possibility to reduce the uncertainty of the extrapolated compressibilities in future. The model uncertainty together with the extrapolation uncertainty and  $u(\kappa_{\text{eff}}(273.16 \text{ K}))$  leads to the overall uncertainty of the extrapolated value of about 0.4% at 80 K.

**5.3 DCGT results near 80 K** Applying DCGT, the thermodynamic temperature  $T$  is deduced from the slope of isotherms at low pressure describing the ideal-gas behavior. This slope is inversely proportional to the sum



**Figure 8** Temperature dependence of estimates for the uncertainty component in DCGT measurements with the gases He, Ne, and Ar that is caused by the uncertainty of the effective compressibilities of capacitors C1 and C2, respectively. The full lines represent the estimates for capacitor C1, and the dashed lines those for capacitor C2. Corresponding to the relative magnitude of the molar compressibilities, the estimates for He are the largest ones, and those for Ar the smallest ones.

$(A_p/RT) + \kappa_{\text{eff}}/3$ , in which  $A_p$  is the molar polarizability of the measuring gas and  $R$  is the molar gas constant [1]. The uncertainty  $u(\kappa_{\text{eff}}(T))$  of the effective compressibility can be, therefore, directly transferred into an uncertainty component  $u_\kappa(T)$  of the measured  $T$  values. This has been done for the two capacitors and three measuring gases applicable for primary thermometry: He ( $A_p \approx 0.5 \text{ cm}^3 \text{ mol}^{-1}$ ), Ne ( $A_p \approx 1 \text{ cm}^3 \text{ mol}^{-1}$ ), Ar ( $A_p \approx 4 \text{ cm}^3 \text{ mol}^{-1}$ ).  $u(\kappa_{\text{eff}}(T))$  contains contributions from  $u(\kappa_{\text{eff}}(273.16 \text{ K}))$  (Section 4.4), the model uncertainty (Section 5.1), and the influence of the input thermophysical quantities (Section 5.2). The obtained uncertainty estimates  $u_\kappa(T)$  are shown in Fig. 8. In all cases, the uncertainty is dominated by  $u(\kappa_{\text{eff}}(273.16 \text{ K}))$  of the determination of  $\kappa_{\text{eff}}$  at the TPW. Nevertheless, the coincidence of DCGT results near 80 K with those got with other primary thermometry methods within the uncertainty limits, as described in Ref. [19], verifies the applicability of the developed extrapolation method for DCGT.

**6 Conclusions** Based on well-known approximate relations between the thermodynamic properties of solids, a method has been developed for extrapolating compressibility data from near room temperature down to 80 K. The method has been tested using the comprehensive experimental literature data for copper. The found relative extrapolation uncertainty is well below 0.1%. In a next step, the method has been applied to a copper–beryllium–cobalt alloy, which is the construction material of measuring capacitors for dielectric-constant gas thermometry, a special kind of primary thermometry for determining thermodynamic temperatures. For this material, the extrapolation uncertainty has been estimated applying Monte-Carlo

simulations. Considering also cross-checks with copper, an estimate of 0.1% has been obtained at 80 K. This uncertainty level is sufficient for performing primary thermometry at the highest level of accuracy. The uncertainty estimates are supported independently, by comparing different results of measurements of thermodynamic temperatures. The developed extrapolation method is, therefore, also useful for other experiments, which require to know the temperature dependence of the compressibility of construction materials.

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