*International Journal of Thermophysics, Vol. 6, No. 5, 1985*

# Aluminum. I. Measurement of the Relative Enthalpy from 273 to 929 K and Derivation of Thermodynamic Functions for Al(s) from 0 K to Its Melting Point

**D. A. Ditmars,[1] C. A. Plint,[2] and R. C. Shukla[2]**

*Received July 2, 1985*

The relative enthalpy of pure, polycrystalline aluminum (NBS Standard Reference Material 44f, for the freezing point of aluminum on IPTS-68) has been measured over the temperature range 273 to 929 K. The enthalpy measurements were made in a precision isothermal phase-change calorimeter and are believed to have an inaccuracy not exceeding 0.2%. Pt-10Rh alloy and quartz glass were used as the encapsulating materials. The enthalpy data for Al(s) and $SiO_2$(l) have been fitted by the method of least squares with cubic polynomial functions of temperature. Heat capacity data for Al(s), derived from these polynomials, have been smoothly merged using a spline technique to the most reliable low-temperature heat capacity data for Al(s) below 273 K. The merged data are compared with corresponding data from the literature as well as with published critical compilations of heat capacity data for Al(s). A new table of thermodynamic functions for Al(s) has been derived. A theoretical interpretation of the results apears in the following paper.

**KEY WORDS:** aluminum; drop calorimetry; enthalpy; heat capacity; quartz; specific heat; thermodynamic functions.

## 1. INTRODUCTION

The most reliable measurements above 273 K of the heat capacity at constant pressure, $C_p$, on solid aluminum have heretofore been considered to be those of Brooks and Bingham [1] (330–893 K), Leadbetter [2] (300–772 K), and Takahashi [3] (300–850 K). Both Brooks and Bingham [1] and Leadbetter [2] have analyzed their data from a Debye-type theory to estimate the anharmonic contribution to the heat capacity at

---

[1] Chemical Thermodynamics Division, National Bureau of Standards, Gaithersburg, Maryland 20899, U.S.A.

[2] Physics Department, Brock University, St. Catharines, Ontario L2S 3Al, Canada.

0195-928X/85/0900-0499$04.50/0

constant volume ($C_{v0}$). Recently, Shukla and Plint [4] carried out a thorough analysis of the two sets of data [1, 2] to extract the anharmonic contribution to the heat capacity of aluminum between its Debye (420 K) and its melting (933 K) temperatures and compared the experimental results with the theoretical anharmonic calculations from a first-principles-type pseudopotential theory. Since it is the heat capacity at constant 0 K volume which is directly calculated in their theoretical treatment [4], it was necessary for Shukla and Plint first to reduce the selected experimental $C_p(T)$ data to $C_{v0}(T)$. This they accomplished [4] by, first, application to the $C_p(T)$ data for aluminum of the thermodynamic relation,

$$C_v(T) = C_p(T) - TV\beta^2 B \tag{1}$$

in which $B$ $[= B(T)]$ is the isothermal bulk modulus, $\beta$ $[= \beta(T)]$ is the isobaric coefficient of volume expansion, $V$ $[= V(T)]$ is the molar volume, and $T$ is the thermodynamic temperature. This was followed by a reduction of $C_v(T, V)$ to $C_v(T, V_0)$, the constant-volume heat capacity referred to the volume at 0 K, using the method of Slater [5], extended by Overton [6], from which a linear electronic contribution was subtracted. Above 700 K, Shukla and Plint also applied corrections for the estimated energy of vacancy formation in aluminum to the reduced $C_{v0}$ data. The theoretical values for both the harmonic and the anharmonic contributions to $C_{v0}(T)$ were calculated [4] employing three different pseudopotentials [7–9]. The most promising potential was found to be a long-range oscillatory potential for which the interaction extended to 28 neighbors, the Dagens–Rasolt–Taylor (DRT) pseudopotential [9]. Comparison of the $C_{v0}(T)$ functions derived from the experimental $C_p$ data of Brooks and Bingham [1] and those of Leadbetter [2] with the three $C_{v0}(T)$ functions derived from each of the three assumed pseudopotentials (cf. Fig. 3 of Ref. 4) indicated a considerable divergence between between the two $C_{v0}(T)$ functions derived from experimental data as well as disagreement of each of these with the theoretical results above 600 K. As a result, Shukla and Plint suggested. the need for an improved, definitive measurement of the $C_p$ of solid aluminum. This work presents just such a $C_p$ measurement. A theoretical analysis of the present $C_p$ results for Al(s) and the evaluation of various anharmonic models is contained in the following paper.

## 2. EXPERIMENTAL

### 2.1. Apparatus

All relative enthalpy measurements were performed with a highly precise and accurate Bunsen ice calorimeter. This is a type of phase-change, receiving calorimeter in which the energy to be measured causes the melting of ice in a constant-volume enclosure containing only $H_2O(l)$, $H_2O(s)$, and $Hg(l)$. The amount of ice melting (or some quantity proportional to this) is then taken as the measure of this energy. The apparatus employed in these NBS heat measurements has been described previously in considerable detail [10–13].

Briefly, an artifact whose relative enthalpy is to be measured is first suspended in the isothermal zone of a controlled-temperature furnace until it reaches a steady temperature. It is then dropped in almost free-fall into a well of the calorimeter. The heat transferred to the calorimeter as the sample cools to the calorimeter temperature (very nearly 273.15 K) melts a portion of the calorimeter ice. The resulting change in volume of the calorimeter's ice–water–mercury system is measured with a sensitive dilatometer. Calibration [11–13] of the calorimeter (i.e., measuring the proportionality between the energy transferred to the calorimeter and the ensuing volume change of the ice–water portion of the system referred to above) is carried out with accurately measured quantities of electrical energy converted to heat in a specially designed electrical heater which fits within the calorimeter well.

## 2.2. Method

In the procedure adopted for the present work, each relative enthalpy datum for a given material of interest is derived in principle from two individual calorimetric measurements. The first measurement is that of the relative enthalpy of the material plus some appropriate encapsulation. The second measurement is that of the relative enthalpy of the encapsulation alone. The difference between these two relative enthalpy data is then the relative enthalpy of the material under the assumption that, in both experiments, the heat lost by the measuring capsules while falling into the calorimeter is identical and, further, that no heat is lost by the encapsulated material during the fall.

The relative enthalpy of Al(s) and of $SiO_2(l)$ (vitreous silica) in the range 273–923 K was derived from such relative enthalpy measurements made on three capsules designated A, B (also called the "blank"), and C. Each of these consisted of a hermetically sealed Pt-10Rh alloy capsule containing materials to be measured. The distribution of *contents* is as follows:

A. 4.97679 g aluminum (NBS SRM-44f) contained within a vitreous silica capsule of mass 4.80481 g;
B. a vitreous silica capsule of mass 4.70086 g; and
C. 0.132835 mol of $\alpha$-$Al_2O_3$ (NBS SRM-720).

In addition, prior relative enthalpy measurements [10] were available for an empty, sealed Pt-10Rh alloy capsule. This empty capsule is designated in the present work capsule SB (also called the "standard blank"). The masses of Pt-10Rh alloy in each of these four capsules were carefully adjusted during fabrication to bring them within a milligram or less of each other.

The relative enthalpies of aluminum, vitreous silica, and α-aluminum oxide were measured by the steps indicated in Fig. 1. Here, the rectangular boxes represent typical individual enthalpy measurements. The upper dashed lines denote the small (<0.01%) additive corrections to the measured enthalpies of artifacts A, B, and C, which account for the difference in Pt-10Rh alloy mass between each of these capsules and capsule SB. The lower dashed line represents an additive correction (<0.8%) to the measured enthalpy of A, which accounts for the difference in $SiO_2$ mass of the contents of capsules A and B. The symbol "sm." indicates smoothed artifact enthalpy data applied to discrete enthalpy data for other artifacts to derive net enthalpy data. The oval boxes represent net enthalpy data for capsule contents.

## 2.3. Samples

The aluminum sample was machined from a bar of NBS Standard Reference Material 44f. This is the NBS SRM for the aluminum freezing point on IPTS-68 [14]. This aluminum is from a batch obtained from Cominco American, Inc. Extensive analyses [15, 16], including semiquantitative spectrochemical, mass-spectrometric, and residual resistance-ratio

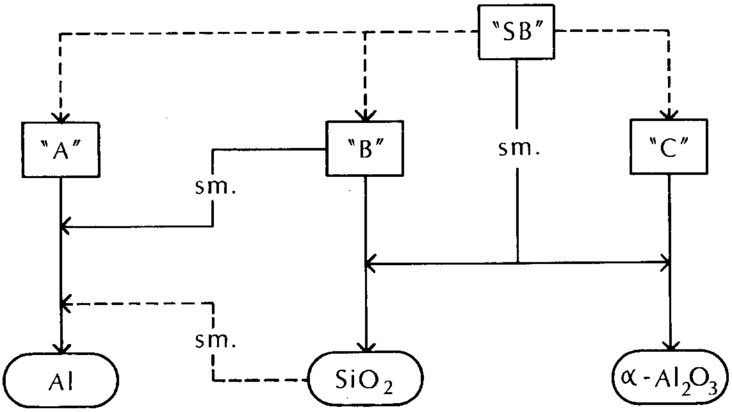

Fig. 1. Derivation of relative enthalpy data for aluminum, $SiO_2$ and α-$Al_2O_3$; cf. text for explanation.

measurements, have shown it to be at least 99.999% pure. The aluminum was contained in a vitreous silica capsule, which was in turn sealed within a Pt-10Rh alloy capsule containing helium at a pressure of a few millimeters Hg. Semiquantitative spectrochemical analysis of the vitreous silica revealed the following impurities: Al, Ba, Ca, Cr, Fe, Mn, Mo, Ni, Sn, Sr, V, and Zr, $<0.05$ mass % each; Ag, B, Cu, K, Li, Mg, Na, and Ti, $<0.02$ mass % each; and Be, $<0.01$ mass %. These impurities were probably present as oxides. No corrections were made to any of the measured heat data for impurity phase contributions.

## 3. RESULTS

### 3.1. Standard Blank Capsule

Original enthalpy data on the standard blank capsule are given in Ref. 10. These data were smoothed by the method of least squares. The equation representing these data is repeated here for convenience:

$$H_t - H_{0^\circ\mathrm{C}} = (4.529744)10^{-8}t^3 + (8.068654)10^{-5}t^2 + (1.9801653)t - (34.94647)\left(\frac{t}{T}\right) \qquad (2)$$

where $H$ is in J, $t$ is in °C, and $T = t + 273.15$ K.

### 3.2. $\alpha$-$Al_2O_3$ SRM

Relative enthalpy data for $\alpha$-$Al_2O_3$ were measured at 373, 573, 773, and 928 K. These data differred from the published enthalpy data for NBS SRM 720 [17] by less than 0.05%, confirming the correct functioning of the calorimeter.

### 3.3. $SiO_2$(l)

The enthalpy data obtained on capsule B (containing only $SiO_2$) are given in order of increasing temperature in columns 2 and 3 in Table I. Here, the chronological sequence of measurement is indicated by the associated indices in column 1. Column 4 also contains a minor ($<0.01$%) additive correction for the Pt-10Rh mass deficiency of B relative to the Pt-10Rh mass of the standard blank. All the data in column 4 were fitted

**Table I.** Enthalpy Data on Vitreous $SiO_2$ in Capsule B

| Index No. | Temperature[a] (K) | Measured gross heat,[b] $H_T - H_{273.15\,K}$ (J) | Measured net heat,[c] $H_T - H_{273.15\,K}$ $(J \cdot mol^{-1})^e$ | Smoothed net heat,[d] $H_T - H_{273.15\,K}$ $(J \cdot mol^{-1})^e$ | Measured net − smoothed net (%) |
|---|---|---|---|---|---|
| 692 | 323.358 | 263.09 | 2209.08 | 2199.28 | +0.45 |
| 690 | 323.508 | 263.68 | 2213.07 | 2206.24 | +0.31 |
| 691 | 323.798 | 264.94 | 2222.56 | 2219.71 | +0.13 |
| 693 | 372.924 | 541.49 | 4604.79 | 4605.45 | −0.01 |
| 719 | 372.991 | 541.78 | 4606.87 | 4608.84 | −0.04 |
| 694 | 373.217 | 543.37 | 4621.90 | 4620.26 | +0.04 |
| 695 | 373.341 | 544.21 | 4629.71 | 4626.53 | +0.07 |
| 680 | 473.359 | 1151.92 | 10000.22 | 10011.89 | −0.12 |
| 681 | 473.457 | 1152.57 | 10006.20 | 10017.45 | −0.11 |
| 683 | 573.256 | 1806.57 | 15922.08 | 15917.04 | +0.03 |
| 682 | 573.275 | 1805.30 | 15905.36 | 15918.21 | −0.08 |
| 697 | 673.761 | 2499.08 | 22268.26 | 22248.42 | +0.09 |
| 696 | 673.980 | 2500.06 | 22275.26 | 22262.57 | +0.06 |
| 704 | 773.641 | 3210.34 | 28826.90 | 28823.78 | +0.01 |
| 705 | 773.664 | 3210.36 | 28826.61 | 28825.32 | +0.00 |
| 712 | 873.38 | 3938.57 | 35562.81 | 35583.03 | −0.06 |
| 711 | 873.46 | 3940.92 | 35590.76 | 35588.51 | +0.01 |
| 710 | 873.52 | 3939,15 | 35566.76 | 35592.21 | −0.07 |
| 718 | 929.77 | 4360.44 | 39481.31 | 39458.36 | +0.06 |
| 717 | 929.84 | 4359.17 | 39463.20 | 39463.11 | +0.00 |
| 716 | 929.92 | 4359.97 | 39471.22 | 39469.05 | +0.01 |

[a] IPTS-68.

[b] Includes correction <0.01% for Pt-10Rh mass deficiency relative to Pt-10Rh in standard blank.

[c] $SiO_2$ mass = 4.70086 g.

[d] Calculated from Eq. (3).

[e] Molecular weight = 60.0848.

by the method of least squares with the following equation for later use in evaluating aluminum net enthalpies:

$$H_t - H_{0°C} = -(8.88561)10^{-7}t^3 + (2.10823)10^{-3}t^2 + (5.91179)t - (2.55669)10^2\left(\frac{t}{T}\right) \tag{3}$$

where $H$ is in $J \cdot mol^{-1}$, $t$ is in °C, and $T = t + 273.15$ K. The residual standard deviation for Eq. (3) is $1.0\ J \cdot mol^{-1}$.

Since the vitreous silica capsules used in these experiments were of uncertain thermal history and were not of particularly high chemical purity, we have used these data (Eq. 3) only to calculate the enthalpy corrections required due to the differing amounts of silica contained in capsules A and B. We note here, however, that the heat capacity data calculated from the enthalpy smoothing function, Eq. (3), were found to differ between 300 and 900 K by less than 0.7% from the data recommended in a recent review of all the literature heat capacity data on $SiO_2(l)$ [18].

### 3.4. Al(s)

The enthalpy data obtained on capsule A (containing $SiO_2$ *and* Al) are given in order of increasing temperature in columns 2 and 3 in Table II. Here, the chronological sequence of measurement is given by the associated indices in column 1. Column 3 contains a minor ($<0.01\%$) additive correction for the Pt-10Rh mass deficiency of A relative to the Pt-10Rh mass of the standard blank. Column 5 [measured net heat of Al(s)] contains a correction ($<0.8\%$) for the $SiO_2$ mass excess of A relative to the $SiO_2$ mass contained in B. The data in column 5 have been expressed on a molar basis using a quantity of Al(s): 0.184452 mol. The aluminum specimen reacted with the quartz encapsulation while still 5.4 K from the anticipated melting point (933.45 K), forming, apparently, a liquid aluminum silicate. Therefore, measurements corresponding to index numbers 734 through 737 and 739 were given zero weight in the final data smoothing. In addition, three of the data (corresponding to index numbers 674, 702, and 729) appeared as outliers and were also given zero weight. All 25 remaining measured net heat data (column 5) were assigned equal weight and fitted by the method of last squares with the following equation:

$$H_T - H_{273.15} = A(T-U)^3 + B(T-U)^2 + C(T-U) + D(T-U)/T \qquad (4)$$

where $H$ is in $J \cdot mol^{-1}$, $T$ is in K, and

$$A = +5.590286 \times 10^{-6}$$
$$B = -1.501113 \times 10^{-3}$$
$$C = +2.801949 \times 10^{+1}$$
$$D = -1.244410 \times 10^{+3}$$
$$U = 273.15$$

The residual standard deviation for Eq. (4) is $6.70\ J \cdot mol^{-1}$.

**Table II.** Enthalpy Data on Al(s) in Capsule A

| Index No. | Temperature[a] (K) | Measured gross heat,[b] $H_T - H_{273.15\,\mathrm{K}}$ (J) | Empty capsule B heat,[c] $H_T - H_{273.15\,\mathrm{K}}$ (J) | Measured Net heat,[d] $H_T - H_{273.15\,\mathrm{K}}$ $(\mathrm{J \cdot mol^{-1}})$[f] | Smoothed net heat,[e] $H_T - H_{273.15\,\mathrm{K}}$ $(\mathrm{J \cdot mol^{-1}})$ | Measured Net[d] – smoothed net (%) |
|---|---|---|---|---|---|---|
| 688 | 323.564 | 492.52 | 263.45 | 1221.20 | 1215.59 | +0.46 |
| 689 | 323.598 | 493.44 | 263.63 | 1225.17 | 1216.42 | +0.72 |
| 687 | 323.851 | 497.04 | 265.01 | 1237.10 | 1222.67 | +1.18 |
| 737[g] | 372.896 | 1001.15 | 541.38 | 2449.43 | 2452.58 | −0.13 |
| 721 | 372.980 | 1002.09 | 541.87 | 2451.85 | 2454.71 | −0.12 |
| 720 | 373.081 | 1002.90 | 542.46 | 2453.01 | 2457.28 | −0.17 |
| 674[h] | 373.525 | 1010.12 | 545.03 | 2477.97 | 2468.58 | +0.38 |
| 675 | 373.591 | 1008.19 | 545.42 | 2465.40 | 2470.26 | −0.20 |
| 736[g] | 423.133 | 1542.81 | 840.41 | 3740.23 | 3746.45 | −0.17 |
| 728 | 423.337 | 1545.18 | 841.71 | 3745.90 | 3751.76 | −0.16 |
| 677 | 473.247 | 2103.27 | 1152.12 | 5062.77 | 5065.14 | −0.05 |
| 678 | 473.389 | 2104.52 | 1153.02 | 5064.59 | 5068.92 | −0.08 |
| 679 | 473.437 | 2104.86 | 1153.33 | 5064.76 | 5070.19 | −0.11 |
| 729[h] | 523.038 | 2672.97 | 1472.92 | 6385.12 | 6400.70 | −0.24 |
| 686 | 573.240 | 3268.49 | 1806.07 | 7779.19 | 7772.81 | +0.08 |
| 684 | 573.261 | 3268.71 | 1806.21 | 7779.60 | 7773.39 | +0.08 |
| 685 | 573.318 | 3268.43 | 1806.59 | 7775.97 | 7774.97 | +0.01 |
| 730 | 573.436 | 3268.24 | 1807.39 | 7770.57 | 7778.22 | −0.10 |
| 731 | 623.312 | 3871.19 | 2146.80 | 9170.23 | 9168.24 | +0.02 |
| 698 | 673.650 | 4491.99 | 2496.75 | 10608.52 | 10600.32 | +0.08 |
| 700 | 673.765 | 4492.86 | 2497.56 | 10608.79 | 10603.63 | +0.05 |
| 699 | 673.804 | 4493.16 | 2497.83 | 10608.91 | 10604.75 | +0.04 |
| 732 | 723.522 | 5116.44 | 2849.81 | 12049.34 | 12050.78 | −0.01 |
| 709 | 773.601 | 5756.74 | 3209.80 | 13537.81 | 13542.08 | −0.03 |
| 703 | 773.789 | 5758.67 | 3211.16 | 13540.78 | 13547.75 | −0.05 |
| 702[h] | 774.064 | 5757.91 | 3213.16 | 13525.69 | 13556.04 | −0.22 |
| 715 | 873.42 | 7070.29 | 3940.44 | 16634.62 | 16632.36 | +0.01 |
| 714 | 873.43 | 7069.24 | 3940.50 | 16628.56 | 16632.65 | −0.02 |
| 713 | 873.46 | 7068.85 | 3940.69 | 16625.43 | 16633.44 | −0.05 |
| 733 | 922.89 | 7738.87 | 4307.42 | 18237.84 | 18229.00 | +0.05 |
| 739[g] | 924.54 | 9768.06 | 4319.68 | 29171.48 | 18282.96 | — |
| 735[g] | 927.65 | 9798.94 | 4342.86 | 29211.24 | 18385.07 | — |
| 734[g] | 928.08 | 8529.95 | 4346.04 | 22313.93 | 18399.10 | — |

[a] IPTS-68.

[b] Includes correction (<0.01%) for Pt-10Rh mass deficiency relative to standard.

[c] Smooth values calculated from Eq. (3).

[d] Includes correction to gross measured heat (<0.8%) for $SiO_2$ mass excess relative to $SiO_2$ in empty capsule B. Al mass = 4.97679 g.

[e] Smooth values calculated from Eq. (4).

[f] Molecular weight = 26.9815.

[g] Datum obtained after melting of aluminum specimen given zero weight in regression analysis.

[h] Datum treated as outlier; given zero weight in regression analysis.

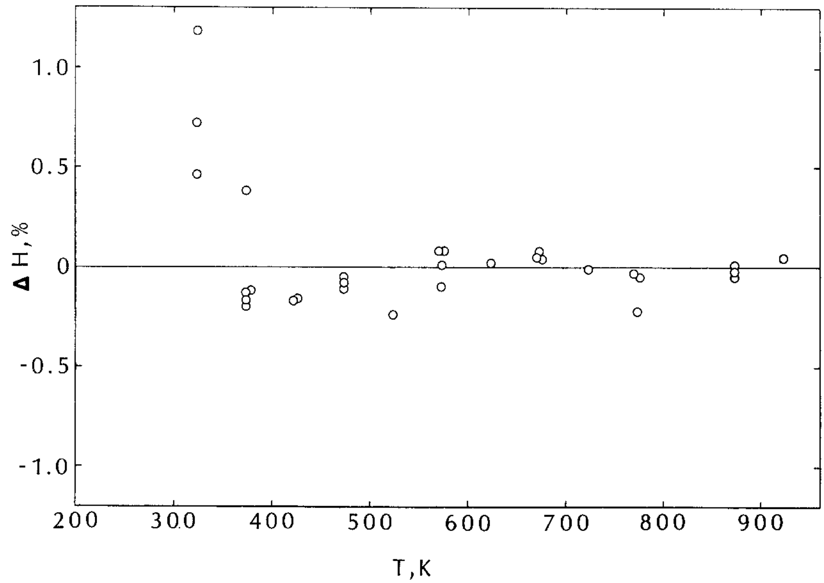

**Fig. 2.** Percentage deviation of present measured enthalpy data for aluminum from adopted smoothing function, Eq. (4).

The percentage deviations of all present measured enthalpy data for aluminum from the adopted smoothing function, Eq. (4), are presented in Fig. 2.

## 4. DERIVATION OF THERMODYNAMIC FUNCTIONS FOR Al(s)

The thermodynamic functions for aluminum (Table AI, Appendix) which provide the starting point for the theoretical analysis of the following paper were calculated from the following relationships using as primary input data a composite heat capacity function.

$$C_p^\circ = \left(\frac{\partial H^\circ}{\partial T}\right)_p \tag{5}$$

$$H_T^\circ - H_{0\,\mathrm{K}}^\circ = \int_0^T C_p^\circ \, dT \tag{6}$$

$$S_T^\circ - S_{0\,\mathrm{K}}^\circ = \int_0^T (C_p^\circ/T) \, dT \tag{7}$$

$$F_T^\circ - H_{0\,\mathrm{K}}^\circ = (H_T^\circ - H_{0\,\mathrm{K}}^\circ) - T(S_T^\circ - S_{0\,\mathrm{K}}^\circ) \tag{8}$$

The composite heat capacity function consisted of three parts. (i) 290 K $\geqslant T$: in this interval the low-temperature data analysis of Chase

[18, 19] was accepted. This, in turn, was based on low-temperature heat capacity measurements of Giauque and Meads [20], Downie and Martin [21], and Berg [22] (all above 4 K) and on equations for the very-low-temperature heat capacity of aluminum due to Phillips [23], Dixon et al. [24], and Hartman et al. [25]. (ii) 933.45 K $\geqslant T \geqslant$ 350: in this interval, heat capacity values were calculated from the present data as summarized in Eq. (4). (iii) 350 K $> T >$ 290; in this interval, heat capacity values were calculated from a cubic spline heat capacity function so constructed as to have values for its derivatives of orders 0, 1, and 2 at 290 and 350 K equal to the values of the corresponding derivatives at 290 and 350 K for the heat capacity functions of intervals i and ii, respectively. The construction of this composite heat capacity function is illustrated in Fig. 3. The enthalpy data between 922.89 K (the highest accepted datum temperature) and the melting point, 933.45 K, have been calculated by assuming the validity of Eq. (4) in this interval. Based on prior experience with the present apparatus and the precision of the present enthalpy data, the enthalpy data in Table AI *above 273.15 K* are believed to have an overall inaccuracy not exceeding 0.2%. The derived heat capacity values are believed to have an

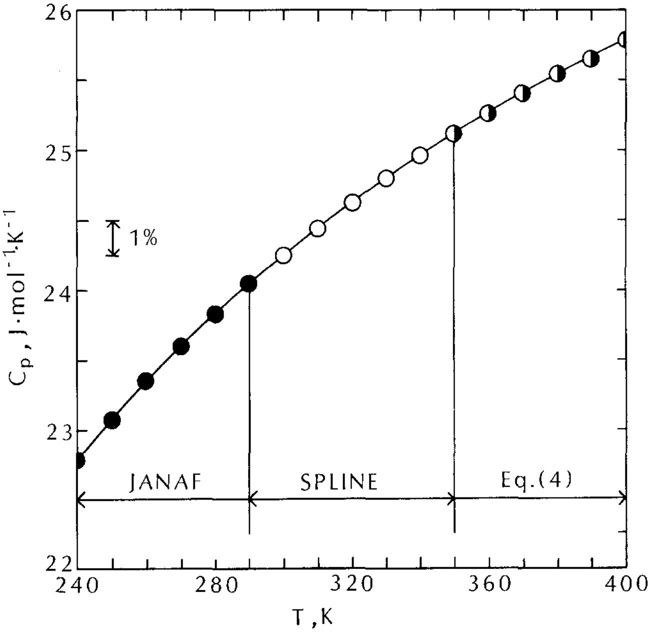

**Fig. 3.** Construction of composite heat capacity function for Al(s) near joining of literature and NBS $C_p$ data. (●) JANAF-evaluated $C_p$ data [18, 19]; (○) spline-merged $C_p$ data of present work; (◑) derived from Eq. (4).

overall inaccuracy not exceeding 0.3%. Note that more significant figures are presented in Table AI than are strictly justified by the accuracy of the data. This is done to facilitate smooth interpolation in the table.

## 5. COMPARISON TO LITERATURE DATA

Only two sets of enthalpy data for aluminum are given in the recent literature [26, 27]. The deviations of these data from the present measured relative enthalpy of aluminum (Table AI) are given in Fig. 4 and show a spread approximately five times that of the present data (cf. Fig. 2). The remaining heat capacity studies of aluminum all measured heat capacity directly, by either continuous- or discrete-heating methods. The deviations of these data from the present derived heat capacity data (Table AI) for aluminum are presented in Fig. 5. The data of Brooks and Bingham [1, 34], presented here as a smooth curve [34], consist of 210 heat capacity measurements made with a continuous-heating adiabatic calorimeter. Of these, 97% deviate by less than 1.5% from the curve and 90% are within 1.2% of it. Takahashi [3] measured the heat capacity of aluminum using a new laser-heating technique. His results above 250 K consist of 107 individual measurements which deviate from the curve

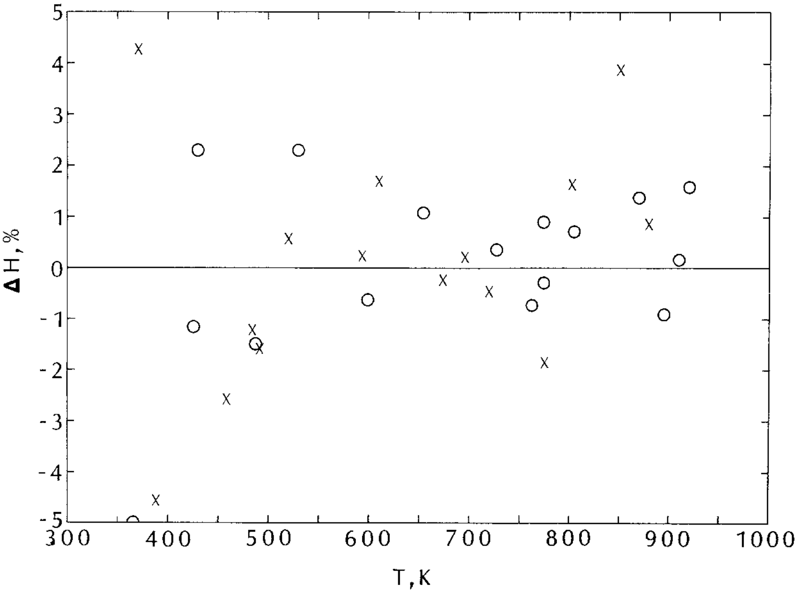

Fig. 4. Percentage deviation of literature enthalpy data for Al(s) from present data. (O) McDonald [26]; (X) Marchidan and Ciopec [27]. Baseline is data given in Table AI, Appendix.

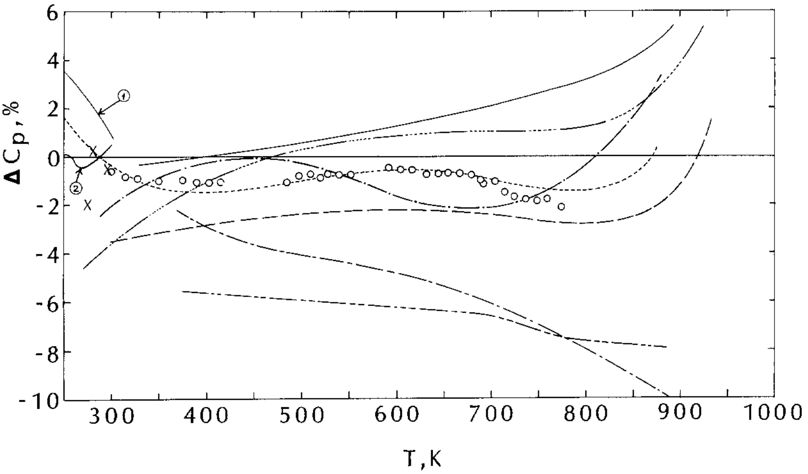

**Fig. 5.** Percentage deviation of literature heat capacity data for Al(s) from present data. (——) Brooks and Bingham [1, 34]; (○) Leadbetter [2]; (---------) Takahashi [3]; ① Giauque and Meads [20]; ② Downie and Martin [21]; (X) Maier and Anderson [33]; (—-—) Umino [28]; (—·—) Seekamp [29]; (—-—) Avramescu [30]; (——-——) Pochapsky [31]; (———) Schmidt et al. [32]. Baseline is data given in Table AI, Appendix.

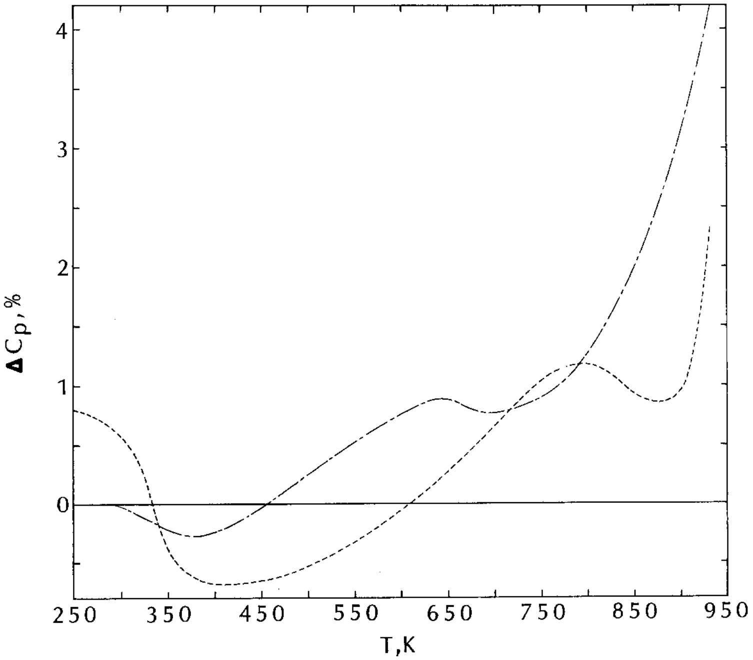

**Fig. 6.** Percentage deviation of critically evaluated heat capacity data compilations for Al(s) from present data. Baseline is data given in Table AI, Appendix. (---------) Hultgren et al. [35]; (—-—) JANAF tables [18, 19].

shown by less than 1%. Leadbetter [2] used a conventional high-temperature adiabatic calorimeter. High-temperature studies, considered of lesser significance because of questionable experimental technique or sparse results, and shown in their smoothed representations are those of Umino [28], Seekamp [29], Avramescu [30], Pochapsky [31], and Schmidt et al. [32]. From heat capacity calorimetry of aluminum in the cryogenic range, results are also available above 250 K from the works of Giauque and Meads [20], Downie and Martin [21], and Maier and Anderson [33]. The heat capacity data of Giauque and Downie scatter by less than 0.1% from their respective smooth representations in the range shown. Figure 6 shows the deviation from the heat capacity values in Table AI for two frequently cited correlations of heat capacity data for solid aluminum [19, 35] which predate the present work. Both are clearly high above 650 K, a direct reflection of the trends in the primary data available to the compilers (cf. Fig. 5).

## APPENDIX

**Table AI.** Thermodynamic Functions of Al(s)

| $T$ (K) | $C_p^\circ$ (J·mol$^{-1}$·K$^{-1}$) | $H_T^\circ - H_0^\circ$ (J·mol$^{-1}$) | $(H_T^\circ - H_0^\circ)/T$ (J·mol$^{-1}$) | $S_T^\circ$ (J·mol$^{-1}$·K$^{-1}$) | $-(G_T^\circ - H_0^\circ)$ (J·mol$^{-1}$) | $-(G_T^\circ - H_0^\circ)/T$ (J·mol$^{-1}$·K$^{-1}$) |
|---|---|---|---|---|---|---|
| 0.00 | 0.000000 | 0.000000 | 0.000000 | 0.000000 | 0.000000 | 0.000000 |
| 1.00 | 0.00138 | 0.000689 | 0.000689 | 0.000858 | 0.000355 | 0.000355 |
| 2.00 | 0.00289 | 0.00280 | 0.00140 | 0.00232 | 0.00192 | 0.000959 |
| 3.00 | 0.00473 | 0.00658 | 0.00219 | 0.00383 | 0.00498 | 0.00166 |
| 4.00 | 0.00699 | 0.0124 | 0.00310 | 0.00549 | 0.00963 | 0.00241 |
| 5.00 | 0.00979 | 0.0207 | 0.00415 | 0.00733 | 0.0160 | 0.00320 |
| 6.00 | 0.0133 | 0.0322 | 0.00537 | 0.00942 | 0.0244 | 0.00406 |
| 7.00 | 0.0177 | 0.0476 | 0.00680 | 0.0118 | 0.0349 | 0.00499 |
| 8.00 | 0.0230 | 0.0679 | 0.00848 | 0.0145 | 0.0481 | 0.00601 |
| 9.00 | 0.0293 | 0.0939 | 0.0104 | 0.0175 | 0.0640 | 0.00711 |
| 10.00 | 0.0369 | 0.127 | 0.0127 | 0.0210 | 0.0833 | 0.00833 |
| 11.00 | 0.0458 | 0.168 | 0.0153 | 0.0249 | 0.106 | 0.00965 |
| 12.00 | 0.0562 | 0.219 | 0.0183 | 0.0294 | 0.133 | 0.0111 |
| 13.00 | 0.0683 | 0.281 | 0.0216 | 0.0343 | 0.165 | 0.0127 |
| 14.00 | 0.0823 | 0.356 | 0.0254 | 0.0399 | 0.202 | 0.0144 |
| 15.00 | 0.0983 | 0.446 | 0.0298 | 0.0461 | 0.245 | 0.0163 |
| 16.00 | 0.117 | 0.554 | 0.0346 | 0.0530 | 0.295 | 0.0184 |
| 17.00 | 0.138 | 0.681 | 0.0400 | 0.0607 | 0.351 | 0.0207 |
| 18.00 | 0.163 | 0.831 | 0.0462 | 0.0693 | 0.416 | 0.0231 |
| 19.00 | 0.191 | 1.008 | 0.0530 | 0.0788 | 0.490 | 0.0258 |

**Table AI.** *(Continued)*

| $T$ (K) | $C_p^\circ$ (J·mol$^{-1}$·K$^{-1}$) | $H_T^\circ - H_0^\circ$ (J·mol$^{-1}$) | $(H_T^\circ - H_0^\circ)/T$ (J·mol$^{-1}$) | $S_T^\circ$ (J·mol$^{-1}$·K$^{-1}$) | $-(G_T^\circ - H_0^\circ)$ (J·mol$^{-1}$) | $-(G_T^\circ - H_0^\circ)/T$ (J·mol$^{-1}$·K$^{-1}$) |
|---|---|---|---|---|---|---|
| 20.00 | 0.223 | 1.214 | 0.0607 | 0.0894 | 0.574 | 0.0287 |
| 21.00 | 0.260 | 1.456 | 0.0693 | 0.101 | 0.669 | 0.0319 |
| 22.00 | 0.301 | 1.736 | 0.0789 | 0.114 | 0.777 | 0.0353 |
| 23.00 | 0.347 | 2.059 | 0.0895 | 0.129 | 0.898 | 0.0391 |
| 24.00 | 0.398 | 2.432 | 0.101 | 0.144 | 1.035 | 0.0431 |
| 25.00 | 0.455 | 2.858 | 0.114 | 0.162 | 1.188 | 0.0475 |
| 26.00 | 0.518 | 3.344 | 0.129 | 0.181 | 1.359 | 0.0523 |
| 27.00 | 0.586 | 3.895 | 0.144 | 0.202 | 1.550 | 0.0574 |
| 28.00 | 0.660 | 4.517 | 0.161 | 0.224 | 1.763 | 0.0630 |
| 29.00 | 0.741 | 5.218 | 0.180 | 0.249 | 1.999 | 0.0689 |
| 30.00 | 0.818 | 5.998 | 0.200 | 0.275 | 2.261 | 0.0754 |
| 40.00 | 2.135 | 20.178 | 0.504 | 0.676 | 6.782 | 0.170 |
| 50.00 | 3.961 | 50.391 | 1.008 | 1.342 | 16.666 | 0.333 |
| 60.00 | 5.919 | 99.766 | 1.663 | 2.237 | 34.395 | 0.573 |
| 70.00 | 7.815 | 168.48 | 2.407 | 3.292 | 61.927 | 0.885 |
| 80.00 | 9.673 | 255.98 | 3.200 | 4.458 | 100.60 | 1.258 |
| 90.00 | 11.429 | 361.61 | 4.018 | 5.700 | 151.34 | 1.682 |
| 100.00 | 12.997 | 483.89 | 4.839 | 6.987 | 214.75 | 2.148 |
| 110.00 | 14.381 | 620.93 | 5.645 | 8.292 | 291.14 | 2.647 |
| 120.00 | 15.597 | 770.95 | 6.425 | 9.597 | 380.59 | 3.172 |
| 130.00 | 16.665 | 932.37 | 7.172 | 10.888 | 483.03 | 3.716 |
| 140.00 | 17.604 | 1103.8 | 7.884 | 12.158 | 598.28 | 4.273 |
| 150.00 | 18.431 | 1284.1 | 8.560 | 13.402 | 726.11 | 4.841 |
| 160.00 | 19.161 | 1472.1 | 9.201 | 14.615 | 866.22 | 5.414 |
| 170.00 | 19.808 | 1667.0 | 9.806 | 15.796 | 1018.3 | 5.990 |
| 180.00 | 20.381 | 1868.0 | 10.378 | 16.945 | 1182.0 | 6.567 |
| 190.00 | 20.890 | 2074.4 | 10.918 | 18.061 | 1357.1 | 7.143 |
| 200.00 | 21.338 | 2285.6 | 11.428 | 19.144 | 1543.2 | 7.716 |
| 210.00 | 21.753 | 2501.1 | 11.910 | 20.195 | 1739.9 | 8.285 |
| 220.00 | 22.133 | 2720.6 | 12.366 | 21.216 | 1947.0 | 8.850 |
| 230.00 | 22.479 | 2943.6 | 12.798 | 22.208 | 2164.1 | 9.409 |
| 240.00 | 22.794 | 3170.0 | 13.208 | 23.171 | 2391.0 | 9.963 |
| 250.00 | 23.084 | 3399.4 | 13.598 | 24.108 | 2627.4 | 10.510 |
| 260.00 | 23.350 | 3631.6 | 13.968 | 25.019 | 2873.1 | 11.050 |
| 270.00 | 23.597 | 3866.4 | 14.320 | 25.904 | 3127.7 | 11.584 |
| 273.15 | 23.671 | 3940.8 | 14.427 | 26.179 | 3209.8 | 11.751 |
| 280.00 | 23.826 | 4103.5 | 14.655 | 26.767 | 3391.1 | 12.111 |
| 290.00 | 24.039 | 4342.8 | 14.975 | 27.607 | 3663.0 | 12.631 |
| 298.15 | 24.209 | 4539.5 | 15.225 | 28.275 | 3890.7 | 13.050 |
| 300.00 | 24.247 | 4584.3 | 15.281 | 28.425 | 3943.2 | 13.144 |

**Table AI.** *(Continued)*

| $T$ (K) | $C_p^\circ$ (J·mol$^{-1}$·K$^{-1}$) | $H_T^\circ - H_0^\circ$ (J·mol$^{-1}$) | $(H_T^\circ - H_0^\circ)/T$ (J·mol$^{-1}$) | $S_T^\circ$ (J·mol$^{-1}$·K$^{-1}$) | $-(G_T^\circ - H_0^\circ)$ (J·mol$^{-1}$) | $-(G_T^\circ - H_0^\circ)/T$ (J·mol$^{-1}$·K$^{-1}$) |
|---|---|---|---|---|---|---|
| 310.00 | 24.441 | 4827.7 | 15.573 | 29.223 | 4231.4 | 13.650 |
| 320.00 | 24.623 | 5073.1 | 15.853 | 30.002 | 4527.6 | 14.149 |
| 330.00 | 24.795 | 5320.2 | 16.122 | 30.763 | 4831.4 | 14.641 |
| 340.00 | 24.958 | 5568.9 | 16.379 | 31.505 | 5142.8 | 15.126 |
| 350.00 | 25.113 | 5819.3 | 16.627 | 32.231 | 5461.5 | 15.604 |
| 360.00 | 25.263 | 6071.2 | 16.864 | 32.941 | 5787.3 | 16.076 |
| 370.00 | 25.403 | 6324.5 | 17.093 | 33.635 | 6120.2 | 16.541 |
| 380.00 | 25.536 | 6579.2 | 17.314 | 34.314 | 6460.0 | 17.000 |
| 390.00 | 25.663 | 6835.2 | 17.526 | 34.979 | 6806.4 | 17.452 |
| 400.00 | 25.784 | 7092.5 | 17.731 | 35.630 | 7159.5 | 17.899 |
| 420.00 | 26.013 | 7610.4 | 18.120 | 36.894 | 7884.9 | 18.774 |
| 440.00 | 26.230 | 8132.9 | 18.484 | 38.109 | 8635.0 | 19.625 |
| 460.00 | 26.438 | 8659.6 | 18.825 | 39.279 | 9409.0 | 20.454 |
| 480.00 | 26.641 | 9190.4 | 19.147 | 40.409 | 10205. | 21.262 |
| 500.00 | 26.842 | 9725.2 | 19.450 | 41.501 | 11025. | 22.050 |
| 520.00 | 27.043 | 10264. | 19.739 | 42.557 | 11865. | 22.819 |
| 540.00 | 27.247 | 10807. | 20.013 | 43.582 | 12727. | 23.569 |
| 560.00 | 27.454 | 11354. | 20.275 | 44.576 | 13608. | 24.301 |
| 580.00 | 27.667 | 11905. | 20.526 | 45.543 | 14510. | 25.017 |
| 600.00 | 27.886 | 12460. | 20.768 | 46.485 | 15430. | 25.717 |
| 620.00 | 28.111 | 13020. | 21.001 | 47.403 | 16369. | 26.402 |
| 640.00 | 28.345 | 13585. | 21.227 | 48.299 | 17326. | 27.072 |
| 660.00 | 28.588 | 14154. | 21.446 | 49.175 | 18301. | 27.729 |
| 680.00 | 28.839 | 14728. | 21.660 | 50.032 | 19293. | 28.372 |
| 700.00 | 29.100 | 15308. | 21.869 | 50.872 | 20302. | 29.003 |
| 720.00 | 29.371 | 15892. | 22.073 | 51.696 | 21328. | 29.622 |
| 740.00 | 29.652 | 16483. | 22.274 | 52.504 | 22370. | 30.230 |
| 760.00 | 29.944 | 17079. | 22.472 | 53.299 | 23428. | 30.826 |
| 780.00 | 30.247 | 17680. | 22.668 | 54.080 | 24501. | 31.413 |
| 800.00 | 30.562 | 18289. | 22.861 | 54.850 | 25591. | 31.989 |
| 820.00 | 30.888 | 18903. | 23.053 | 55.609 | 26695. | 32.556 |
| 840.00 | 31.225 | 19524. | 23.243 | 56.357 | 27815. | 33.114 |
| 860.00 | 31.574 | 20152. | 23.433 | 57.096 | 28950. | 33.663 |
| 880.00 | 31.935 | 20787. | 23.622 | 57.826 | 30099. | 34.204 |
| 900.00 | 32.308 | 21430. | 23.811 | 58.548 | 31263. | 34.737 |
| 920.00 | 32.693 | 22080. | 24.000 | 59.262 | 32441. | 35.262 |
| 933.45 | 32.959 | 22521. | 24.127 | 59.738 | 33241. | 35.611 |

## ACKNOWLEDGMENTS

A portion of this work was supported by the U.S. Air Force Office of Scientific Research (AFOSR). R. C. Shukla acknowledges the support of the Natural Sciences and Engineering Research Council of Canada.

## REFERENCES

1. C. R. Brooks and R. E. Bingham, *J. Phys. Chem. Solids* **29**:1553 (1968).
2. A. J. Leadbetter, *J. Phys. C (Proc. Phys. Soc.)* **1**:1481 (1968).
3. Y. Takahashi, Private communication, 4 Dec. 1981.
4. R. C. Shukla and C. A. Plint, *Int. J. Thermophys.* **1**:299 (1980).
5. J. C. Slater, *Introduction to Chemical Physics* (McGraw–Hill, New York, 1939), Chap. XIII.
6. W. C. Overton, *J. Chem. Phys.* **37**:2975 (1962).
7. W. A. Harrison, *Pseudopotentials in the Theory of Metals* (Benjamin, New York, 1966).
8. N. W. Ashcroft, *Phys. Lett.* **23**:48 (1966).
9. L. Dagens, M. Rasolt, and R. Taylor, *Phys. Rev.* **B11**:2726 (1975).
10. D. A. Ditmars and T. B. Douglas, *J. Res. Natl. Bur. Stand. (U.S.)* **75A**:401 (1971).
11. T. B. Douglas and E. G. King, in *Experimental Thermodynamics, Vol. I. Calorimetry of Non-Reacting Systems*, J. P. McCullough and D. W. Scott, eds., (Butterworths, London, 1968); cf. also NBS Special Publication No. 33, p. 181 (1970).
12. D. A. Ditmars, *Int. J. Appl. Rad. Isotopes* **27**:469 (1976).
13. D. C. Ginnings, T. B. Douglas, and A. F. Ball, *J. Res. Natl. Bur. Stand (U.S.)* **45**:23 (1950) (RP2110).
14. NBS Certificate: Standard Reference Material 44f, Aluminum, 5 Apr. 1973.
15. G. T. Furukawa, *J. Res. Natl. Bur. Stand. (U.S.)* **78A**:477 (1974).
16. G. T. Furukawa, J. L. Riddle, W. R. Bigge, and E. R. Pfeiffer, *Application of Some Metal SRM's as Thermometric Fixed Points*, NBS Special Publication 260-77 (1982).
17. D. A. Ditmars, S. Ishihara, S. S. Chang, and G. Bernstein, *J. Res. Nat. Burl. Stand. (U.S.)* **87**(2):159 (1982).
18. Dow Chemical Co. Thermal Research Group (M. W. Chase, private communication), 7 July 1981.
19. *JANAF Thermochemical Data*, Table (Al), 30 June 1979 (obtainable from the Dow Chemical Co., 1707 Building, Midland, MI 48640).
20. W. F. Giauque and P. F. Meads, *J. Am. Chem. Soc.* **63**:1897 (1941).
21. D. B. Downie and J. F. Martin, *J. Chem. Thermodyn.* **12**:779 (1980).
22. W. T. Berg, *Phys. Rev.* **167**:583 (1968).
23. N. E. Phillips, *Phys. Rev.* **114**:676 (1959).
24. M. Dixon, F. E. Hoare, T. M. Holden, and D. E. Moody, *Proc. R. Soc. Lond.* **285**:561 (1965).
25. W. M. Hartmann, H. V. Culbert, and R. P. Heubener, *Phys. Rev. B* **1**:1486 (1970).
26. R. A. McDonald, *J. Chem. Eng. Data* **12**:115 (1967).
27. D. I. Marchidan and M. Ciopec, *Rev. Roum. Chim.* **15**:1005 (1970).
28. S. Umino, *Sci. Rep. Tohoku Imp. Univ. (Ser. 1)* **15**:597 (1926).
29. H. Seekamp, *Z. Anorg. Allg. Chem.* **195**:345 (1931).
30. A. Avramescu, *Z. Tech. Phys.* **20**:213 (1939).
31. T. E. Pochapsky, *Acta Metall.* **1**:747 (1953).

32. U. Schmidt, O. Vollmer, and R. Kohlhaas, *Z. Naturforsch.* **25a**:1258 (1970).
33. C. G. Maier and C. T. Anderson, *J. Chem. Phys.* **2**:513 (1934).
34. C. R. Brooks, Private communication, 9 Dec. 1970.
35. R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, K. K. Kelley, and D. D. Wagman, in *Selected Values of the Thermodynamic Properties of the Elements* (American Society for Metals, Metals Park, OH, 1973).