(4.7) and (4.8) in checking analytic behavior as a function of temperature and coupling. If we assume that for some sufficiently high temperature the whole scheme is self-consistent, poles of $S_R(\omega)S_A(\omega)$ in the lower half-plane must be poles of $S_R(\omega)$. Hence we simply track the zeros of $G_R(\omega)G_A(\omega)+16\pi^2\rho^2S(S+1)$ as a function of temperature. If they always stay in their original (high T) half-plane the system will behave smoothly. It appears that this must be the case, since $G_R(\omega^*)=G_A^*(\omega)$ so on the real axis the expression has the form $|G|^2+16\pi^2\rho^2S(S+1)$ and clearly cannot be zero.

5. POSSIBLE SOLUTION OF NAGAOKA'S EQUATION

Notice here the similarity to the pole positions found by Hamann, discussed above [see (3.10)]. The poles are at

$$X_R^2(\omega)+16\pi^2\rho^2S(S+1)=0, \qquad (5.1)$$

where $X_R(\omega)=\ln\omega+iT/iT_k$. $X_R(\omega)$ is quite similar to $G_R(\omega)$, since $\Psi(z)\approx\ln(z-\frac{1}{2})$ and $\ln(-iT_k)$ corresponds to the physics factor R. In Hamann's case, it is easy to show that the poles of X_R stay below the real axis.

Since Hamann's approximation was essentially to replace $H_R(\omega)$ [Eq. (2.1)] by $-\gamma X_R(\omega)$ [Eq. (3.9)], and since solutions to Nagaoka's equation are restricted by Eq. (3.5) to having an analytic structure very similar to those discussed in the preceding section, it seems reasonable to suppose that the exact solution to Nagaoka's equation, noting (5.1) and writing the equation analogous to (4.8), is given by

$$S_R(\omega)S_A(\omega)=\frac{H_R(\omega)H_A(\omega)}{H_R(\omega)H_A(\omega)+16\pi^2\rho^2S(S+1)\gamma^2}. \qquad (5.2)$$

This satisfies (3.5), has the same smooth behavior as (4.8) as a function of temperature, and would give a spin-flip amplitude $\tau_R=S_RH_R^{-1}=K_R^{-1}$ [see (3.8)].

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Heat Capacity of Scandium from 1 to 23°K*

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The heat capacity C_p of a well-characterized, polycrystalline scandium sample was measured from 0.9 to 23°K. The results are in reasonable agreement with previous measurements below 4°K, except that a small anomalous addendum to the heat capacity was detected, which is believed to be due to small concentrations of magnetic impurities in the sample. The results below 8.4°K after correction for the effect of impurities could be represented by the equation $C_p=\gamma T+(12R\pi^4/5)(T/\Theta)^3$, where $\gamma=10.66\pm0.10$ mJ deg^{-2}(g at.)$^{-1}$ and $\Theta=359.5\pm4.2$°K. A table of smoothed heat capacities and thermodynamic functions for scandium at selected temperatures between 5 and 298.15°K is presented.

INTRODUCTION

The heat capacity of scandium has been determined by Montgomery and Pells[1] between 1.7 and 4°K. They evaluated the electronic and lattice parameters to be $\gamma=11.3\pm0.1$ mJ deg^{-2} (g at.)$^{-1}$ and $\Theta=470\pm80$°K, respectively. Lynam, Scurlock, and Wray[2] have measured the heat capacity of the same scandium specimen between 0.5 and 3°K and reported $\gamma=10.9\pm0.1$ mJ deg^{-2} (g at.)$^{-1}$ and $\Theta=344\pm25$°K. The rather large uncertainties in the values for Θ reflect the fact that the lattice contribution to the heat capacity is only 3.4% of the total at 3°K and 6% at 4°K. The latter authors also measured a second specimen of scandium in another apparatus from 0.15 to 0.5°K and obtained anomalous results which could not be interpreted satisfactorily.[2] Heat-capacity data for scandium in the temperature range 51 to 298°K have been reported by Weller and Kelley.[3]

In this paper we report the heat capacity of a well-characterized sample of scandium from 1 to 23°K. Below 5°K a small anomaly was found which is probably due to impurities. However, it was possible to obtain a reliable value for γ and to obtain a much better estimate of the lattice heat capacity and Debye Θ from the new data above 3°K. Some thermodynamic properties of scandium at selected temperatures between 5 and 298.15°K have been calculated from the present heat-capacity data at the lower temperatures and from the data given by Weller and Kelley[3] at the higher temperatures.

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* Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[1] H. Montgomery and G. P. Pells, Proc. Phys. Soc. (London) 78, 622 (1961).

[2] P. Lynam, R. G. Scurlock, and E. M. Wray, in *Proceedings of the 9th International Conference on Low Temperature Physics*, edited by J. G. Daunt, D. O. Edwards, F. J. Milford, and M. Yaqub (Plenum Press, New York, 1965), Part B, pp. 905–907.

[3] W. W. Weller and K. K. Kelley, U. S. Bureau of Mines, Report of Investigations, No. 5984, 1962 (unpublished).

EXPERIMENTAL

The scandium metal was a polycrystalline vacuum-distilled sample which was obtained from Johnson, Matthey and Company. The oxygen content was determined to be 630±30 parts per million by the inert-gas fusion technique. The results of a spectrographic analysis gave the following results in parts per million: Ag, <100; Al, 20; As, <1000; B, <10; Ba, <1; Be, <1; Bi, <100; Ca, <20; Cd, <10; Ce, 100; Co, <10; Cr, 20; Cs, <10; Cu, 20; Dy, <5; Er, <5; Eu, <5; Fe, 100; Ga, <2; Gd, 100; Ho, <5; K, 100; La, 100; Li, <1; Mn, <5; Mo, <100; Na, 10; Nd, <20; Ni, 10; Pb, <10; Pr, <20; Rb, <10; Sb, <100; Si, 10; Sm, <10; Sn, <100; Sr, <1; Ta, 60; Tb, <5; Ti, <100; Tm, <10; V, <10; Y, 10; Zn, <20; Zr, <100. The above values are accurate to about a factor of 2. By neutron-activation analysis the following rare-earth impurities were found in parts per million: La, 50; Ce, 47; Nd, 6; Gd, 65; Eu, <0.3; Tb, 0.9; Ho, 0.1; Tm, $\leqslant 2$; Yb, $\leqslant 3.5$; Lu, 6.7. These values are reliable to ±25%. Finally, the iron content was determined by chemical analysis to be 167±5 parts per million.

The heat-capacity measurements were made by the isothermal method with an apparatus which has been described in an earlier publication.[4] That publication gives the details of the measuring techniques, of the calibrated platinum-encapsulated germanium resistor used to measure the temperatures, and of the calorimeter design (See Fig. 4 of Ref. 4).

The scandium crystals were broken into pieces 1 to 4 mm on an edge and then pressed in a die at 1-kbar pressure to form a specimen which fits inside the calorimeter. The technique is similar to one used in this laboratory to prepare powdered samples for calorimetric measurements,[5] except that in this case a copper capsule was not used. After pressing, each of two specimens prepared as described above was cleaned of surface contamination by light filing with a new Swiss file, and they were then annealed at 700°C for 1 h in an evacuated quartz tube at a pressure of 1×10^{-6} mm Hg. The two specimens were put into the calorimeter, which was soldered shut *in vacuo*.[5] Thermal contact between the scandium and the calorimeter was achieved by Apiezon T grease between the contacting surfaces[4,5] so that no helium exchange gas was required for any of the measurements. The mass of the scandium sample was 14.535 g *in vacuo*.

RESULTS

The experimental heat-capacity data are presented in order of ascending temperature in Table I. The temperature rise for each run is approximately 10% of the average temperature. These values have been corrected for the finite temperature increments but have not been corrected for impurities in the sample. The heat capacity of the empty calorimeter and of the Apiezon T grease[6] were determined in separate experiments. The estimated probable error in the heat capacities is ±0.2%. This error estimate is based in part on the calibration of the germanium thermometer[4] and on the heat-capacity data obtained for pure copper[4] with this apparatus.

DISCUSSION

The results below 9°K are plotted as C_p/T versus T^2 in Fig. 1, where the circles represent the experimental heat capacities and the squares, through which a straight line is drawn, represent the experimental heat capacities less a correction for impurities estimated in the following manner. The magnetic, electronic, and crystalline properties of scandium metal do not indicate that an anomalous contribution to the heat capacity is to be expected within the temperature range of this experiment. Accordingly, we have analyzed the data with the assumption that the heat capacity of pure scandium below 9°K can be represented by an electronic term proportional to T and a lattice term proportional to T^3 and by a term to represent the excess heat capacity, C_{excess}, which is caused by impurities in the scandium.

It was found that the experimental data between 2.9

TABLE I. Experimental heat-capacity results for scandium. At. wt = 44.956. Units are $\bar{T}$ in °K and C_p in mJ(°K)$^{-1}$(g at.)$^{-1}$.

$\bar{T}$	C_p	$\bar{T}$	C_p	$\bar{T}$	C_p
0.899	10.80	2.439	27.72	7.952	106.0
0.997	11.91	2.523	28.65	8.312	112.7
1.001	11.96	2.686	30.47	8.803	122.8
1.099	13.05	2.781	31.53	9.100	129.0
1.105	13.11	2.965	33.62	9.719	142.9
1.207	14.22	3.063	34.73	9.976	148.8
1.212	14.28	3.265	37.04	10.52	162.3
1.328	15.55	3.372	38.28	10.94	173.0
1.328	15.54	3.580	40.73	11.57	190.2
1.415	16.43	3.704	42.21	11.96	201.8
1.462	16.99	3.921	44.85	12.74	226.6
1.463	16.95	4.071	46.73	13.13	240.1
1.466	17.04	4.304	49.63	14.00	272.7
1.561	18.01	4.512	52.33	14.37	287.7
1.615	18.66	4.724	55.14	15.12	320.5
1.618	18.63	4.740	55.32	15.34	330.8
1.619	18.69	4.929	57.95	16.50	389.8
1.730	19.87	5.196	61.54	16.88	411.6
1.783	20.44	5.381	64.23	16.94	414.9
1.783	20.49	5.726	69.12	18.02	481.1
1.786	20.53	5.918	72.05	18.59	520.6
1.925	22.02	6.301	77.83	19.75	607.2
1.982	22.60	6.525	81.45	20.48	668.9
2.097	23.89	6.918	87.71	21.69	781.3
2.203	25.11	7.200	92.64	22.62	880.1
2.277	25.87	7.587	99.28		

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[4] D. W. Osborne, H. E. Flotow, and F. Schreiner, Rev. Sci. Instr. 38, 159 (1967).

[5] H. E. Flotow and D. W. Osborne, Rev. Sci. Instr. 37, 1414 (1966).

[6] E. F. Westrum, Jr., C. Chou, D. W. Osborne, and H. E. Flotow, Cryogenics 7, 43 (1967).

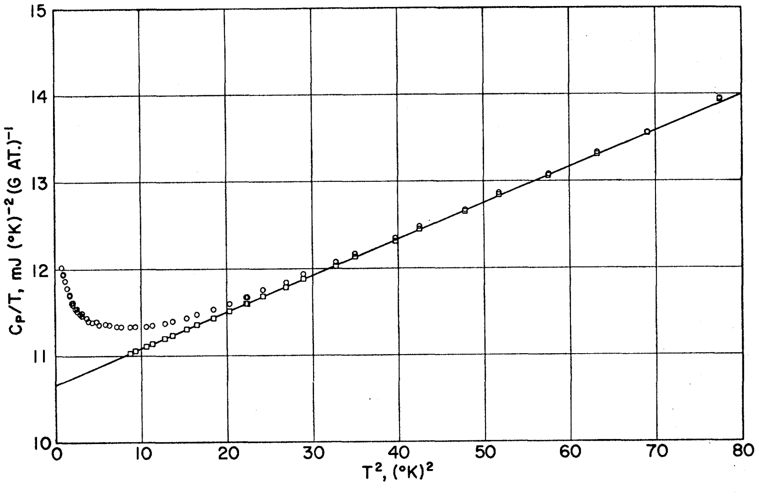

FIG. 1. Heat capacity of scandium, plotted as C_p/T versus T^2. Circle: (Observed C_p)/T; Square: (Observed $C_p - 8.0 \times T^{-2}$)/T.

and 8.4°K can be fitted by the equation

$$C_p = 10.66\,T + 0.04182\,T^3 + 8.0\,T^{-2}\ \text{mJ deg}^{-1}\ (\text{g at. Sc})^{-1}, \quad (1)$$

with a standard deviation of 0.055%. C_{excess} in this equation is given by the term $8.0\,T^{-2}$. The straight line drawn through the squares in Fig. 1 represents the first two terms on the right side of Eq. (1).

A plot of C_{excess} versus T, where

$$C_{\text{excess}} = C_p - 10.66\,T - 0.04182\,T^3\ \text{mJ deg}^{-1}\ (\text{g at. Sc})^{-1}, \quad (2)$$

is presented in Fig. 2. It is seen that C_{excess} reaches a maximum value of 1.3 mJ deg^{-1} (g at. Sc)$^{-1}$ near 1.2°K and then diminishes rapidly at higher temperatures. This, of course, is the behavior expected if C_{excess} is due to the impurities and is a Schottky function or a sum of Schottky functions. The dashed portion of the curve from 0 to 0.9°K in Fig. 2 was calculated from a 2-level Schottky function with a maximum of 1.3 mJ deg^{-1} (g at. Sc)$^{-1}$ at 1.2°K. The excess entropy due to the impurities was evaluated from the Schottky function up to 0.9°K, from a graphical integration of a plot of C_{excess} versus T between 0.9 and 3°K, and by an integration of $8.0\ \text{T}^{-2}$ at higher temperatures. The estimated excess entropies in mJ deg^{-1} (g at. Sc)$^{-1}$ are 0.5 from 0 to 0.9°K, 1.4 from 0.9 to 3°K, and 0.4 from 3°K to ∞, for a total of 2.3±0.5.

Estimated Effect of Impurities

Although neither theoretical nor experimental information allows a quantitative calculation of the excess heat capacity at the lowest temperatures, an examination of possible effects from known impurity concentrations may be helpful to suggest the course of future investigations.

The largest impurity is 630 parts per million of oxygen. Microscopic examination of the scandium crystals revealed a white deposit, which one can reasonably assume to be mainly Sc_2O_3. If all of the oxygen impurity is present as Sc_2O_3, about 0.12 at. % of the scandium would be in the form of the oxide. The heat capacity of Sc_2O_3 has not been measured below 50°K, but no anomaly is expected at low temperatures. The correction for this impurity is probably small (<0.2%) and has therefore been neglected.

Rare-earth impurities probably give rise to Schottky anomalies in the heat capacity, with an associated entropy of

$$S = k \ln(2J+1)\ \text{per atom}, \quad (3)$$

where k is Boltzmann's constant and J is the degeneracy of the ground level of the free ion, assumed to be M^{+2} for europium and ytterbium and M^{+3} for all the other rare earths. Thus, Phillips and Matthias[7] have measured the heat capacity of $La_{0.993}Gd_{0.007}$ and have concluded that the entropy associated with the gadolin-

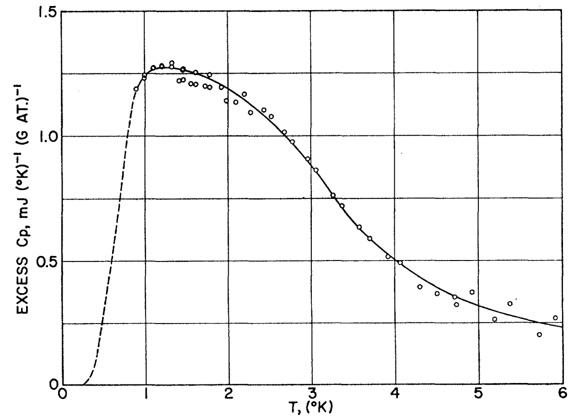

FIG. 2. Excess heat capacity [see text, Eq. (2)] of the present sample of scandium. The dashed curve shows the extrapolation assumed from 0.9 to 0°K in calculating the excess entropy.

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[7] N. E. Phillips and B. T. Matthias, Phys. Rev. **121**, 105 (1961).

ium is within experimental error equal to the expected value, namely 0.007 Rln8 per mole of alloy. The calculated excess entropy for the present sample is 0.21 mJ deg^{-1} (g at. Sc)$^{-1}$ due to 47-ppm cerium, 0.32 due to 65-ppm gadolinium, 0.12 due to 20-ppm praseodymium (the limit of detection of this element), and 0.16 due to all the other rare earths, a total of 0.81±0.2 mJ deg^{-1} (g at. Sc)$^{-1}$.

Thus, there is a discrepancy of 1.5±0.7 mJ deg^{-1} (g at. Sc)$^{-1}$ between the observed excess entropy 2.3±0.5, and the calculated entropy due to the rare-earth impurities, 0.81±0.2 mJ deg^{-1} (g at. Sc)$^{-1}$. The only other known impurity in the sample which could possibly account for this discrepancy is the 167 ppm of iron. However, the effect of dilute solid solutions of iron in scandium is uncertain, because the theory does not give an unambiguous answer and the available experimental results are conflicting. Clogston *et al.*[8] have reported that the solution of 1 at.% iron in scandium greatly increases the magnetic susceptibility at low temperatures and that this observation suggests a large localized moment in the alloy. On the other hand, Blum and Freeman[9] have reported that Mössbauer experiments on 1% Fe^{57} in scandium over the range 1.5 to 300°K have shown no localized moments. If the discrepancy of 1.5±0.7 mJ deg^{-1} (g at. Sc)$^{-1}$ is attributed solely to the 167-ppm Fe, the value of J for iron calculated from Eq. (3) is 1.4, corresponding to a localized magnetic moment of 2.8 Bohr magnetons per iron atom if $g=2$, with a factor of 2 uncertainty.

It is apparent that the properties of scandium at low temperatures are grossly modified by the presence of parts per million of magnetic impurities. A systematic study of the thermal, electronic, and magnetic properties of very pure scandium and of scandium alloyed with small and varying amounts of magnetic metals would be of considerable interest. However, such studies must await much purer scandium metal than is presently available.

TABLE II. Comparison of reported values of γ and Θ_0 for scandium. Units are mJ deg^{-2} (g at.)$^{-1}$ for γ and °K of Θ_0. Method 1: low-temperature calorimetry. Method 2: elastic moduli from sound attenuation at low temperature.

Authors	Method	γ	Θ_0
Montgomery and Pells[a]	1	11.3 ±0.1	470 ±80
Lynam *et al.*[b]	1	10.9 ±0.1	344 ±25
Present work	1	10.66±0.10	359.5± 4.2
Fisher and Dever[c]	2	···	360 ± 2

[a] Reference 1.
[b] Reference 2, specimen I.
[c] Reference 11.

γ and Θ_0 of Scandium

The present work indicates that up to 8.4°K the heat capacity of pure scandium is given by the first two terms on the right-hand side of Eq. (1). The coefficient γ in the familiar expression for the contribution of the conduction electrons to the heat capacity (γT) is therefore 10.66±0.10 mJ deg^{-2} (g at.)$^{-1}$. The Debye Θ near 0°K, designated as Θ_0, is obtained from the coefficient of the second term, A_2, by means of the relation $\Theta_0=(12R\pi^4/5)^{1/3}A_2^{-1/3}$, and is found to be 359.5 ±4.2°K. The uncertainties indicated were estimated by considering the effect of the impurity correction. A least-squares fit of the uncorrected C_p data from 4.5 to 8.4°K with only linear and cubic terms gives $\gamma=10.76$ mJ deg^{-2} (g at.)$^{-1}$ and $A_2=0.04041$ mJ deg^{-4} (g at.)$^{-1}$ or $\Theta_0=363.7$°K.

Table II presents a comparison of the values of γ and Θ_0 from the present work with those obtained by others. The values of γ are in reasonably good agreement, although the differences are somewhat greater than the sum of the estimated uncertainties assigned by the observers. As expected from the similarity in electronic structures, γ for scandium is nearly the same as for yttrium (10.2±0.1)[1] and lanthanum (10.1±0.25).[10] The value of Θ_0 obtained by Fisher and Dever[11] from measurements of the elastic moduli at low temperatures agrees very well with that obtained in the present work. As remarked earlier, the calorimetric determinations of Θ_0 by Montgomery and Pells[1] and by Lynam *et al.*[2] were much less accurate because in scandium the lattice contribution is a rather small fraction of the total heat capacity at 3 or 4°K.

A plot of the Debye Θ for scandium as a function of temperature is shown in Fig. 3. The circles are values which were calculated from our data above 2.9°K by subtracting the first and last terms of Eq. (1) (i.e., the contributions of the conduction electrons and of the impurities, respectively) from the observed C_p and

TABLE III. Some thermodynamic properties of scandium at selected temperatures.

T (°K)	C_p J(°K)$^{-1}$ (g at.)$^{-1}$	$S°$ J(°K)$^{-1}$ (g at.)$^{-1}$	$(H°-H_0°)/T$ J(°K)$^{-1}$ (g at.)$^{-1}$	$-(G°-H_0°)/T$ J(°K)$^{-1}$ (g at.)$^{-1}$
5	0.0585	0.0551	0.0280	0.0271
10	0.1492	0.1206	0.0638	0.0568
15	0.3151	0.2090	0.1170	0.0920
20	0.6286	0.3380	0.2017	0.1363
25	1.168	0.5315	0.3368	0.1947
50	6.54	2.819	1.974	0.845
100	16.44	10.74	6.99	3.75
150	21.10	18.40	11.01	7.39
200	23.40	24.83	13.86	10.97
250	24.65	30.19	15.90	14.29
298.15	25.58	34.61	17.39	17.22
	±0.08	±0.10	±0.05	±0.05

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[8] A. M. Clogston, B. T. Matthias, M. Peter, H. J. Williams, E. Corenzwit, and R. C. Sherwood, Phys. Rev. **125**, 541 (1962).

[9] N. Blum and A. J. Freeman, Rev. Mod. Phys. **36**, 406 (1964); N. Blum, National Magnet Laboratory Report No. NML-64-2, 1964 (unpublished).

[10] A. Berman, M. W. Zemansky, and H. A. Boorse, Phys. Rev. **109**, 70 (1958).

[11] E. Fisher and D. Dever (private communication).

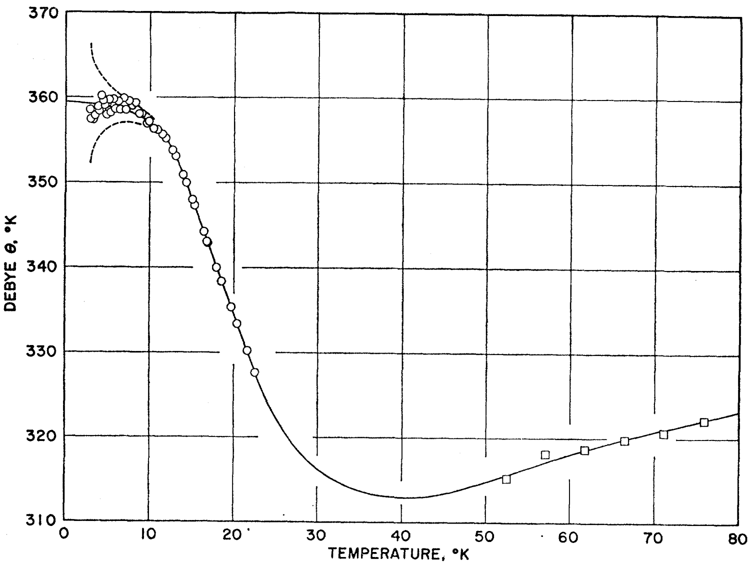

FIG. 3. Debye Θ's for scandium. No correction was made for (C_p-C_v). All the C_p data were corrected for the contribution of the conduction electrons by subtracting 10.66×T mJ deg^{-1} (g at.)$^{-1}$. Circles: present data, corrected also for impurities by subtracting 8.0×T^{-2} mJ deg^{-1} (g at.)$^{-1}$ from the observed C_p; Squares: data of Weller and Kelley. The dashed lines show the effect of $\pm\frac{1}{2}\%$ change in C_p.

fitting each residual with a Debye heat-capacity function. The dotted lines below 10°K show the variation of Θ caused by a ±0.5% change in the value of C_p. The squares were obtained from the data of Weller and Kelley[3] after subtraction of 10.66 T mJ deg^{-1} (g at.)$^{-1}$. No C_p-C_v correction was made because no values for the thermal expansion of scandium are available. However, it is likely that the C_p-C_v correction will have a negligible effect on the values of Θ below 20°K. Above 20°K the Θ's calculated in this manner may differ appreciably from the actual Θ's, but the plot is useful for estimating the heat capacity in the region 23 to 51°K where there are no experimental data.

THERMODYNAMIC FUNCTIONS

The heat capacity C_p, entropy $S°$, enthalpy function $(H°-H_0°)/T$, and Gibbs energy function $(G°-H_0°)/T$ are given at selected temperatures between 5 and 298.15°K in Table III. Entries up to 25°K were calculated from the present C_p data less the correction 8.0 T^{-2} mJ deg^{-1} (g at.)$^{-1}$ for impurities. Between 25 and 50°K values of C_p were calculated at intervals of 2.5°K from the graphical values of Θ (Fig. 3), plus the electronic heat capacity γT. Above 50°K the experimental data of Weller and Kelley[3] were used. The calculations were performed by using a computer to fit the heat-capacity points to two polynomials, one for $T<45$°K (standard deviation 0.090%) and the other for $T\geqslant45$°K (standard deviation 0.150%). The tabulated values of C_p between 50 and 298.15°K differ by less than the estimated experimental error of 0.3% from those given by Weller and Kelley. They reported a value for $S°$ at 298.15°K of 34.31±0.25 J deg^{-1} (g at.)$^{-1}$, which is based upon heat capacities measured above 51°K and extrapolated below 51°K. The smaller uncertainty assigned to our tabulated value, ±0.10, reflects a smaller uncertainty in the entropy at 51°K.

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