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# LOW TEMPERATURE HEAT CAPACITY OF SCANDIUM AND SCANDIUM ALLOYS†

T.-W. E. Tsang, K. A. Gschneidner, Jr.,* and F. A. Schmidt

Ames Laboratory-ERDA and Department of
Materials Science and Engineering
Iowa State University, Ames, IA. 50011, U.S.A.



## ABSTRACT

The heat capacity of several scandium samples containing between 1.6 and 10,000 ppm atomic Fe was measured from 1 to 20 K. Samples containing more than 30 ppm Fe exhibit an anomaly between 1 and 1.5 K, but two scandium samples containing less than 5 ppm Fe did not show any anomalies. For these two samples the weighted values for $\gamma$ and $\theta_D$ are: $10.340 \pm 0.018$ mJ/g-at. K$^2$ and $346.1 \pm 0.9$ K, respectively.

## INTRODUCTION

Many of the low temperature properties of "pure" scandium have been measured and in general there is considerable variation in the reported values, suggesting that they are quite sensitive to impurities.[1] In particular the electronic specific heat constant, $\gamma$, was reported to vary from 10.3 to 11.3 mJ/g-at. K$^2$ and the Debye temperature, $\theta_D$, from 344 to 470 K,[1-7] see Table I. Such large variations, especially for the Debye temperature are most unusual. Furthermore, Lynam et al.[4] and Isaacs[7] noted a departure from linearity in the C/T vs T$^2$ plot below 2 K which had the appearance of the high-temperature tail of a Schottky anomaly and Flotow and Osborne[5] showed a similar anomaly below 5 K. Because of the wide variation in the heat capacity

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results it was felt that measurements on high purity, well characterized scandium were needed.

## ROUTINELY PREPARED SCANDIUM

Scandium prepared at the Ames Laboratory usually contains between 30 and 60 ppm atomic iron unless extra special precautions are taken. The heat capacity of a sample containing 30 ppm iron was found to exhibit an anomaly at 1.1 K in a plot of C/T vs $T^2$, Fig. 1. A least square fit of the data above 1.5 K in the linear region yielded $\gamma$ = 10.426 mJ/g-at. K and $\theta_D$ = 391.4 K. The $\gamma$ value is nearly the same as the lowest value previously reported, but the $\theta_D$ value falls near the middle of the range of values reported (see Table I). Similar results (Table I) were obtained with scandium samples containing larger amounts of iron (51, 111, 5000 and 10 000 ppm atomic), except that the temperature of the peak of the anomaly increased with higher iron contents. Since the two alloys with 5000 and 10 000 ppm iron contained a second phase, presumably $Sc_3Fe$[8], these results are not given in Table I. Furthermore, $\gamma$ and especially $\theta_D$ varied inconsistently from sample to sample and with heat treatment. The facts that anomalies were found in the heat capacity measurements made below 1.5 K and that $\theta_D$ varied by as much as 36%, suggested that a magnetic impurity, presumably iron or possibly iron plus others, are interacting with the scandium giving rise to these effects. Further discussion of these results will be deferred until later.

## ELECTROTRANSPORTED SCANDIUM

An attempt was made to purify scandium by solid state electrotransport since it was thought that the iron group metals might be removed from the scandium along with non-metallic impurities. Two scandium samples were purified by electrotransport, one in the high temperature bcc β-Sc region (sample ET-1) and one in the hcp α-Sc region (sample ET-2).[9] The heat capacity of the second Sc sample is shown in Fig. 1 and the results for both samples are given in Table I. Also noted in Table I are the Fe contents of the two samples. Neither sample exhibited an anomaly down to the lowest temperature, and the results are nearly identical. The weighted average values for the two are $\gamma = 10.340 \pm 0.018$ mJ/g-at. K$^2$ and $\theta_D = 346.1 \pm 0.9$ K.

The temperature dependence of the Debye temperature of the electrotransported Sc remains constant up to 10 K before it begins to decrease with increasing temperature. The temperature range over which $\theta_D$ is constant is about twice as large as that found for many other metallic substances.

IRON INTERACTIONS IN SCANDIUM

The interaction of iron atoms over large interatomic distances (10 - 20 neighbors) has been observed previously in dilute Fe alloys. If the exchange coupling between the magnetic ion (Fe) and the conduction electrons is positive the conduction electrons spins are aligned parallel to the magnetic spin(s) and this polarization can lead to ferromagnetism at very low concentrations and to giant magnetic moments, e.g. Fe in Pd.[10] If, however, the exchange coupling is negative the conduction electron spins are aligned antiparallel to the magnetic spin(s) and this gives rise to the Kondo effect, e.g. Fe in Cu.[10] Magnetic susceptibility measurements of Sc samples containing as low as 10 to 20 ppm atomic Fe and up to saturation with Fe ($\leq 0.1$ at.%) show no evidence for giant moments.[1,11] Resistivity measurements of a number of Sc samples by 13 different investigators containing various amounts of iron show no evidence for a Kondo minimum down to the lowest temperatures measured, generally 4 K,[1] with the possible exception of the results of Spedding *et al.*[12] These authors presented data which might possibly be interpreted to show a very shallow broad minimum at 8 K, but the depth of the minimum is about the same as the precision of the measurements. The previous heat capacity data which show a low temperature anomaly, however, have been interpreted in terms of magnetic ordering of impurities in Sc. Thus until the present measurements the nature of the interaction of magnetic impurities in Sc was an open question.

The heat capacity data on electrotransport purified Sc give us the intrinsic values for Sc metal and enable us to establish a basis for evaluating the effect of the Fe impurity. The excess heat capacity, $\Delta C$, was obtained by subtracting the heat capacity of the electrotransported

Sc from the measured heat capacity of the various Sc samples which contained more than 30 ppm atomic Fe. The $\Delta C$ vs. temperature curve, as one might guess from Fig. 1, shows a more-or-less symmetrical bump about the temperature of the maximum found in C/T vs. $T^2$ plot (see Fig. 1). According to the Kondo-Appelbaum theory[10] $\Delta C$ should have a $T \ln T_K/T$ dependence for $T \ll T_K$. A plot of $\Delta C$ vs. $T \ln T_K/T$ for the heat capacity data below the peak temperature in the C/T vs. $T^2$ plot is shown in Fig. 2 and is seen to be in accord with theory. The Kondo temperature, $T_K$, is assumed to be 8 K, and is based on the resistivity results of Spedding et al.[12] Thus the heat capacity measurements are in accord with the existence of a Kondo system in Sc containing small amounts of Fe impurity, and support the magnetic susceptibility data, which indicate the absence of giant moments, and also the resistivity data, which possibly show the existence of a Kondo minimum.

## OTHER ALLOYING STUDIES

At the time of writing this manuscript, work has begun on the study of the effect of electron concentration on the $\gamma$ and $\theta_D$ of Sc. Alloys containing Mg to lower the electron concentration and Zr to increase the electron concentration are being examined. These results will be described at the time of the Conference.


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TABLE I. Heat Capacity Results on Various Scandium Samples

| $\gamma$ $\left(\frac{mJ}{g\text{-at. }K^2}\right)$ | $\theta_D$ (K) | Fe Conc. (at. ppm) | Temp. Range (K) | Ref. |
|---|---|---|---|---|
| 11.3 ± 0.1 | 470 ± 80 | 56 | 1.7 - 4.2 | 2 |
| 10.3 | - | - | - | 3 |
| 10.9 ± 0.1 | 344 ± 25 | 60 | 0.15 - 3 | 4 |
| 10.66 ± 0.1 | 359.5 ± 4 | 80 | 1 - 23 | 5 |
| 10.72 ± 0.03 | 425.6 ± 14 | 95 | 1.14 - 4.2 | 6 |
| 10.72 ± 0.05 | 359 ± 9 | 40 | 0.5 - 4.2 | 7 |
| 10.426 ± 0.012 | 391.4 ± 1.5 | 30 | 1.03 - 19.7 | a |
| 10.243 ± 0.028 | 340.4 ± 1.4 | 51 | 1.16 - 20.0 | a |
| 10.313 ± 0.008 | 344.7 ± 0.8 | 1.6 | 1.09 - 20.0 | ET-1[b] |
| 10.354 ± 0.004 | 346.8 ± 0.4 | <5 | 1.06 - 20.5 | ET-2[b] |

[a]This study, routinely prepared Sc.

[b]This study, electrotransported Sc.

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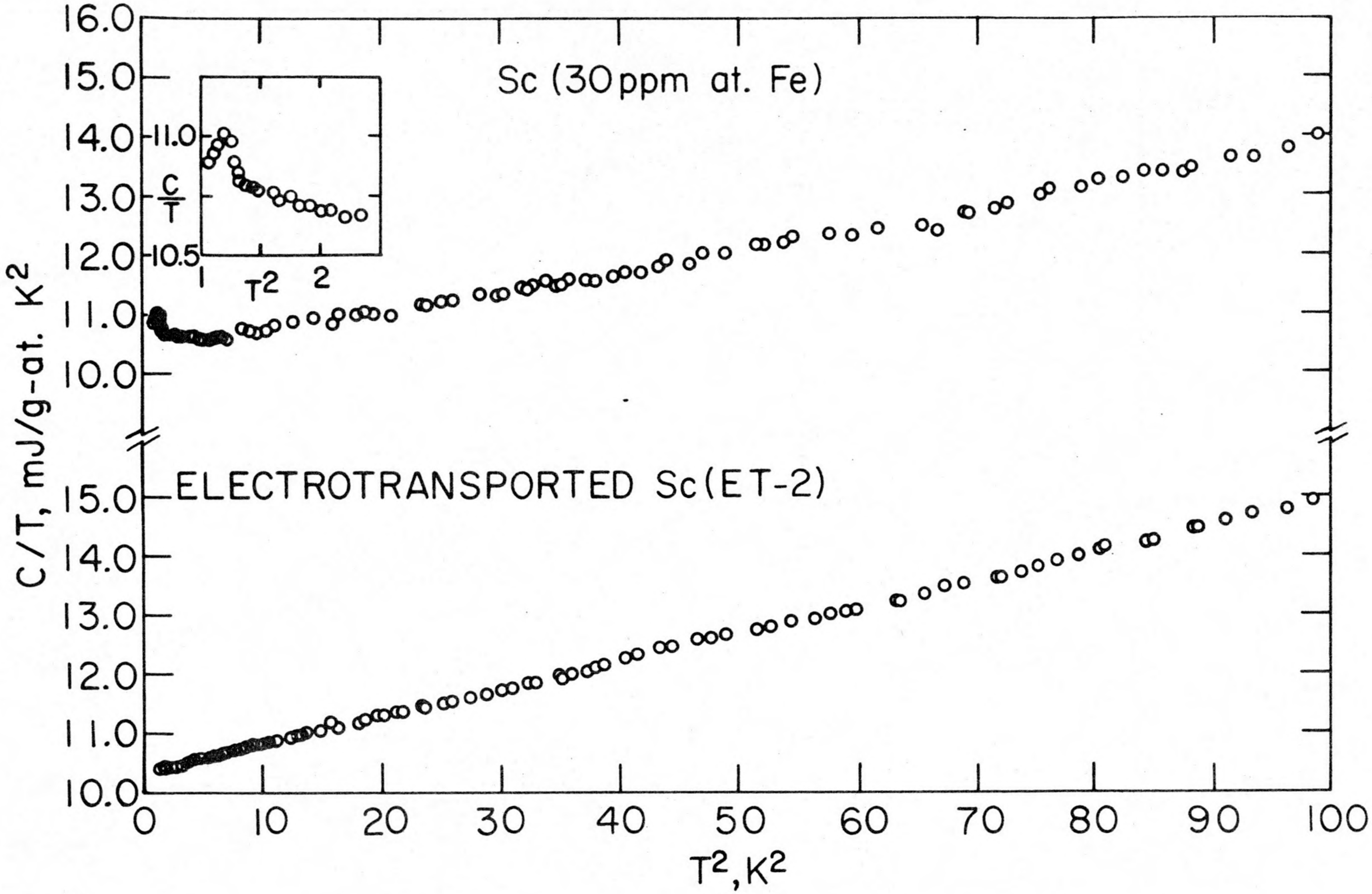


Fig. 1. The heat capacity of a scandium sample containing 30 ppm atomic Fe (upper plot) and of a scandium sample purified by electrotransport and containing less than 5 ppm atomic Fe (lower plot).

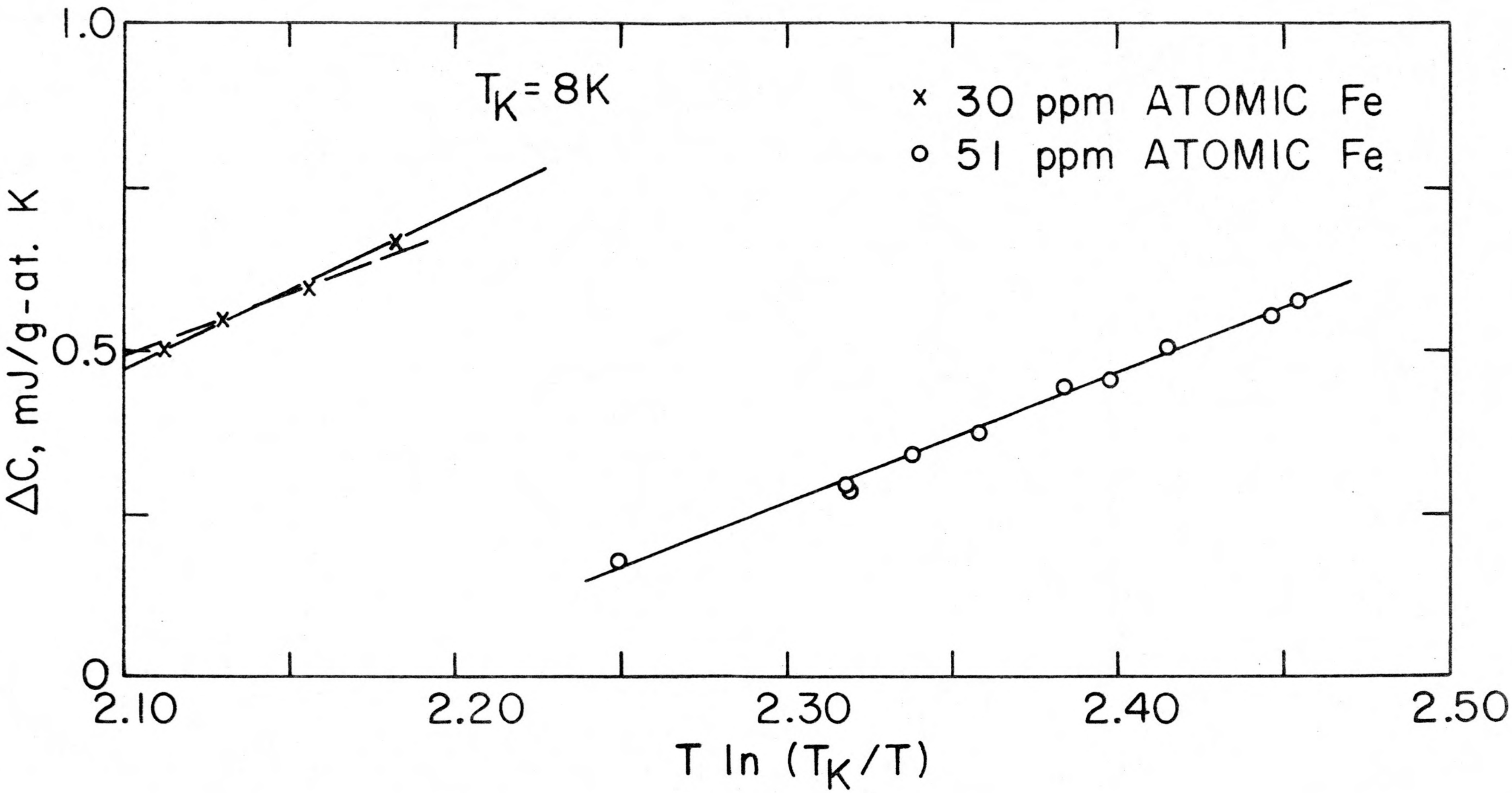


Fig. 2. The excess heat capacity of two scandium samples containing small amounts of iron impurities is plotted against the Kondo-Appelbaum[10] function. The dashed line drawn through the points for the 30 ppm Fe sample has the same slope as that drawn through the points for the 51 ppm atomic Fe sample.