Magnetic susceptibility and heat capacity of Ce_2Sn_5

S. K. Dhar,* Karl A. Gschneidner, Jr., and O. D. McMasters

Ames Laboratory, Iowa State University, Ames, Iowa 50011
and Department of Materials Science and Engineering, Iowa State University, Ames, Iowa 50011

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Low-temperature (1.5—20 K) high-field (0—10 T) heat-capacity and magnetic-susceptibility (1.5—300 K) studies have been carried out on Ce_2Sn_5. These studies reveal that Ce_2Sn_5 orders magnetically at 3 K and exhibits Curie-Weiss behavior above 120 K with $p_{eff}=2.56\mu_B$ indicating that Ce is trivalent in Ce_2Sn_5. The peak in the heat capacity is suppressed in applied magnetic fields and disappears completely at high fields (>5.4 T) which suggests that the magnetic ordering is antiferromagnetic or ferrimagnetic. The magnetic entropy is about 42% of the theoretical expected entropy for a doublet ground state. The coefficient of the electronic heat capacity, which was derived from extrapolation of the heat-capacity data above the ordering temperature, is 22 mJ/mole-Ce K^2. It is suggested that both magnetic Ruderman-Kittel-Kasuya-Yosida and Kondo exchange interactions coexist in this compound.

I. INTRODUCTION

Cerium and tin form a number of binary intermetallic compounds with each other. In a recent reexamination of the Ce-Sn system by metallographic and x-ray techniques, Borzone et al.[1] have confirmed the existence of nine phases. These range from the cerium-rich Ce_3Sn to the tin-rich $CeSn_3$ composition. Of all these compounds $CeSn_3$ has undoubtedly been studied the most. Interest in understanding the physical properties of $CeSn_3$ arises because this compound is considered to be a typical example of that class of cerium and other related materials where the f level is in proximity to the Fermi level. The strong $4f$—conduction-band hybridization in cerium materials leads to a host of anomalous physical properties such as an enhanced electronic-specific-heat constant, large values of the coefficient of the T^2 term in the electrical resistivity at low temperatures, and, quite often, a nonmagnetic ground state. Theoretical efforts to understand the anomalous behavior of such systems have invoked the concepts of interconfigurational fluctuations, Kondo spin fluctuations, Fermi-liquid ground state, etc.[2]

Ikeda et al. found that in an external magnetic field spin fluctuations could be quenched in $CeSn_3$.[3] A drastic reduction of the electronic-specific-heat constant, γ, by about 25% from its zero-field value was observed at 10 T. Such a large decrease of γ prompted a later study where slightly-off-stoichiometric samples were also studied.[4] The results for $CeSn_3$ and tin-rich compositions (up to $CeSn_{3.05}$) corroborated the earlier results; a peak in the heat capacity at ~3 K was observed in tin-deficient $CeSn_{2.98}$ and $CeSn_{2.95}$, the magnitude of the anomaly being larger in $CeSn_{2.95}$. A metallographic examination of these two alloys showed the presence of small amounts of a second phase which suggested that the anomalous behavior may be due to this extra phase. In the Ce-Sn phase system Ce_2Sn_5 is the first tin-deficient compound after $CeSn_3$. On the premise that the occurrence of Ce_2Sn_5 as a parasitic phase in tin-deficient $CeSn_3$ is most

likely, we have carried out the present work on the magnetic susceptibility and heat capacity of Ce_2Sn_5.

II. EXPERIMENTAL

A 29-g sample of Ce_2Sn_5 was prepared by arc melting the stoichiometric amounts of 99.9 at. %—pure Ce and 99.99 at. %—pure Sn in an argon atmosphere. The major impurities in the Ce were the nonmetallic elements H (690 atomic ppm), O (230), N (200), F (88), C (70), and Cl (20). The major metallic impurities were Pt (16 atomic ppm), Ni and Ta (7 each), and Fe (3), while the major rare-earth impurities were Tb (4 atomic ppm), La (3), and Yb (< 10). Weight losses after repeated remeltings were found to be negligible (0.7%). Metallographic examination revealed that the as-arc-melted alloy contained some second phase, and thus the alloy was heat treated for 2 weeks at 1100 °C. A reexamination showed that the alloy was single phase after this heat treatment.

Magnetic susceptibility measurements were carried out in the temperature range 1.5—300 K, in an external magnetic field of 1.8 T, by using the Faraday technique.[5] However, the field dependence of the susceptibility was measured from 0.8 to 1.8 T at 1.5, 4.2, 77, and 295 K. The heat capacity was measured using an isolation heat-pulse-type, semiadiabatic low-temperature calorimeter with a mechanical heat switch. The temperature was monitored by using a germanium resistance thermometer, which had been calibrated at magnetic fields of 0, 2.5, 5.3, 7.5, and 9.8 T.[6]

III. RESULTS AND DISCUSSION

Figure 1 shows a plot of X_m^{-1} as a function of temperature. A Curie-Weiss behavior is observed in the temperature range 120—300 K with an effective paramagnetic moment of $2.56\mu_B$ per Ce ion, which is nearly the same as the free trivalent Ce moment ($2.54\mu_B$), and Θ_p of -43 K. The deviation from the Curie-Weiss behavior at low tem-
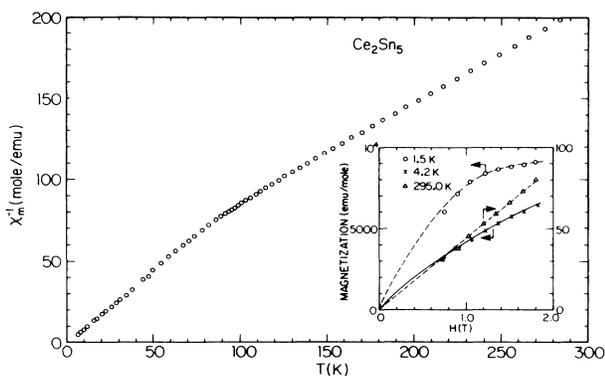
FIG. 1. The inverse magnetic susceptibility versus temperature for Ce$_2$Sn$_5$. The inset shows the magnetization versus field behavior at 1.5, 4.2, and 295 K.

peratures is presumably caused by the crystal fields which lift the degeneracy of the Ce^{3+}, $J = \frac{5}{2}$ state.

The magnetization measurements at 295.0, 4.2, and 1.5 K are depicted in the lower right inset of Fig. 1. The magnetic ordering as inferred from heat-capacity measurements in applied fields (discussed below) is probably antiferromagnetic-ferrimagnetic in nature. It is possible that the near saturation observed in magnetization at 1.5 K is due to the limited range of the field strength used and that the magnetization may increase further for higher applied fields. In a field of 1.8 T we obtain a saturation moment of 0.8μ_B at 1.5 K.

Considering the antiferromagnetic nature of the transition it is possible that the magnetization at 1.5 K could exhibit a spin-flop behavior at fields lower than 0.8 T. Due to some experimental limitation which restricted our lowest field measurements to 0.8 T, we could not check this possibility.

The magnetization versus field curve at 4.2 K exhibits a slight curvature, around $H = 1$ T. Above 1 T the curve is linear and the highest fields extrapolation to $H = 0$ gives a magnetization which corresponds to an effective moment of 0.17μ_B, suggesting that some of the Ce atoms have ordered magnetically at this temperature in applied fields of ~1.8 T. This is consistent with the heat-capacity results (see below) in which some field-induced magnetic interactions occur above the ordering temperature for $H > 1$ T.

Often large negative values of Θ_p are observed for compounds where the Ce ions exhibit valence fluctuations or Kondo behavior at low temperatures. In such compounds a rough measure of the Kondo temperature is given by the relation $T_K \cong \frac{1}{4}\Theta_p$.[7] In the present case we believe that the large negative paramagnetic Curie temperature arises primarily because of the limited temperature range of X^{-1} versus T fit. However, on grounds of entropy considerations (discussed below) we believe Kondo interactions are also present in Ce$_2$Sn$_5$. At low temperatures the magnetization at 1.8 T rises rapidly but does not exhibit a sharp peak at the transition. Rather it tends to flatten below 3 K. The absence of a sharp feature in the magnetization at the transition is presumably due to the large magnetic

field (1.8 T) used in these measurements which tends to destroy the antiferromagnetic interaction between the Ce ions (see below).

The heat capacity as a function of temperature is plotted in Fig. 2. A peak in the heat capacity is observed at $H = 0$, which is lowered to 2.75 K in an applied field of $H = 2.5$ T. Correlated with the susceptibility results mentioned above, the anomaly in the heat capacity can be attributed to the occurrence of a magnetic transition. It is observed that the external field (1) suppresses the peak in the heat capacity such that it becomes an inflection point at 5.3 T and completely disappears at higher fields, and (2) shifts the entropy of the transition to higher temperatures. This indicates that the magnetic transition observed in zero field is presumably antiferromagnetic or ferrimagnetic in nature. It may be noted that even in a field of 2.5 T the heat-capacity peak is appreciably reduced and the transition broadened, which is consistent with the low-temperature susceptibility measurements noted above.

It is of interest to calculate the magnetic entropy, S_M, involved in a magnetic transition. For this it is necessary to subtract the normal electronic and lattice contributions to the heat capacity. For cerium compounds these two are often approximated to be the same as that of isotypic La compound. In the present context we are not aware of any information as regards La$_2$Sn$_5$. Therefore, we have estimated the electronic and lattice contribution from a linear plot of C/T versus T^2 above the magnetic ordering temperature in the range 9–16 K (see Fig. 3). Considering that the T^3 approximation to lattice heat capacity is valid only for temperatures below $\Theta_D/50$, we realize the limitation of the procedure adopted here, but it is our only recourse. The resultant parameters are $\gamma = 6.2 \pm 0.2$ mJ/g atom K^2 (22 mJ/mole-Ce K^2), $\beta = 0.438 \pm 0.001$ mJ/g atom K^4, and $\Theta_D = 164$ K. Since the Debye temperature for CeSn$_3$ is 252 K,[3] this suggests that the calculated value for Θ_D for Ce$_2$Sn$_5$ is too small by perhaps as much as 50%, and thus in turn β is too large and γ is too small. However, the actual choice of β and γ to estimate
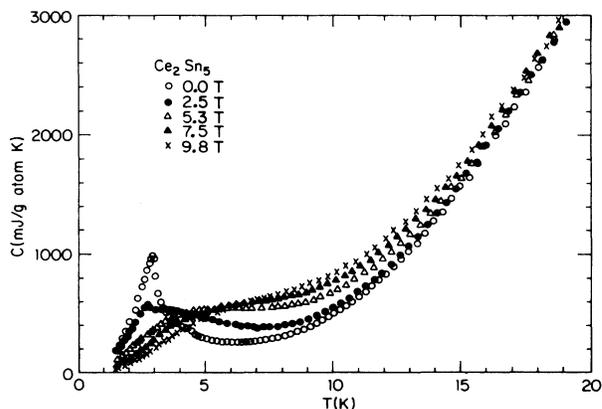

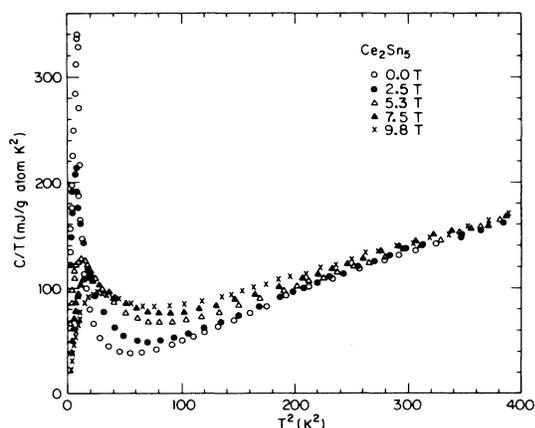FIG. 2. The heat capacity of Ce$_2$Sn$_5$ from 1.4 to 19 K at five fields.

FIG. 3. C/T versus T^2 plot for Ce$_2$Sn$_5$ over the temperature range of 1.4—19 K at five fields.

TABLE I. The magnetic entropy associated with the magnetic ordering of Ce$_2$Sn$_5$ as a function of external magnetic field.

Field (T)	S_M (mJ/mole-Ce K)	Temperature range (K)
0	2400	0—9.8
2.5	2470	0—17.2
5.3	2410	0—17.2
7.5	> 2360[a]	0—18.0
9.8	> 2220[a]	0—17.9
R ln2	5762	

[a]As seen in either Figs. 2 or 3, there appears to be a small amount of magnetic entropy above 19 K, our highest measured heat capacity.

the electronic and lattice contributions does not have a great effect on the resultant magnetic entropies and using the above numbers ($\gamma = 6.2$ and $\beta = 0.438$) may over estimate S_M by a few percent (< 5%).

The magnetic entropies were calculated from 0 to ~19 K, the highest temperature for which a heat-capacity value was measured. Below 1.5 K the heat-capacity curves were extrapolated in a C/T versus T plot to meet the C/T axis at the intercept γ.

In the above analysis the Schottky contribution to the heat capacity, which arises from the crystal-field splitting of Ce^{3+}, $J = \frac{5}{2}$ state, has not been taken into account. The Schottky contribution can be calculated provided the crystal-field level structure is known. In the present context, where such an information is not available, we have calculated the Schottky contribution for two cases of level splitting of 100 and 150 K, respectively, between the ground state and the first excited state. We were governed in our choice of these numbers by the observation that the susceptibility deviates from Curie-Weiss behavior at about 90 K. Since the crystal symmetry is orthorhombic,[1,8] we have taken both the levels to be doublets. Repeating the fitting procedure mentioned above, after subtracting the Schottky term, we get the following values: $\gamma = 11.7 \pm 0.1$ mJ/g atom K^2, $\beta = 0.373 \pm 0.001$ mJ/g atom K^4 for level splitting of 100 K and $\gamma = 6.9 \pm 0.1$ mJ/g atom K^2, $\beta = 0.430 \pm 0.001$ mJ/g atom K^4 for level splitting of 150 K. In the latter case the values are nearly the same as those calculated above for no Schottky contribution. When we compare the susceptibilities of Ce$_2$Sn$_5$ and CePt$_2$ breaks from the high-temperature straight lines of a $1/\chi$ versus T occur at 90 and 30 K, respectively. For CePt$_2$, the level splitting between the ground state and excited state is 216 K (Ref. 9) and thus a crystal-field splitting of 150 K or larger is not unreasonable and thus we have ignored any Schottky contribution to the heat capacity below 20 K.

The resultant magnetic entropies are shown in Table I, where it is seen that the magnitude of the entropy in-

volved per mole of Ce (there are two moles of Ce in Ce$_2$Sn$_5$) is found to be ~42% of the expected $S_M = R$ ln2 for a doublet ground state. Magnetization measurements at 1.5 K also favors this presumption.

One possible explanation for this missing entropy is that the degeneracy of the doublet is not completely lifted in the temperature range of our measurements and that there are other magnetic transitions at lower temperatures such as found by Vining and Shelton[10] in Er$_2$Fe$_3$Si$_5$. This, however, is not too likely, since one should find appreciable contributions to the heat capacity when a substance orders up to ~5 K above the ordering temperature. Since none were found below 20 K (except for that associated with the 3-K magnetic transition) and since our lowest experimentally attained temperature is 1.5 K we can rule out this explanation.

It is possible that there are competing Kondo and Ruderman-Kittel-Kasuya-Yosida (RKKY) interactions in Ce$_2$Sn$_5$ and that the Kondo interactions partially lift the degeneracy of the ground-state doublet. A γ value of 6.2 mJ/g atom K^2 (~22 mJ/mole-Ce K^2) would tend to support the view that Kondo interactions are operative in this compound. A large value of γ is one of the characteristic features of Kondo or valence-fluctuation compounds.[2] For example, the nonmagnetic Kondo compound CeAl$_3$ has a γ of ~1.6 J/mole-Ce K^2 (Ref. 11) while CeAl$_2$ which orders magnetically and has Kondo interactions possess a γ of ~135 mJ/mole-Ce K^2 (Ref. 12). Depending upon the relative strengths of two interactions (RKKY and Kondo exchange) the enhanced γ of the magnetically ordering Ce compound may therefore vary over a wide range. It may be mentioned that in an extensive study of La$_x$Ce$_{1-x}$Ge$_2$ by Mori et al.[13] using resistivity, heat-capacity, and susceptibility techniques, competing Kondo interactions have been shown to significantly lower the magnetic entropy below that expected for a doublet ground state. It would be of interest to study the resistivity behavior of Ce$_2$Sn$_5$.

The entropy under the heat-capacity anomaly in the Sn-deficient CeSn$_3$ sample, CeSn$_{2.95}$, is ~5% of that observed in Ce$_2$Sn$_5$ which is consistent with amount of second phase Ce$_2$Sn$_5$ observed metallographically in the CeSn$_{2.95}$ alloy.

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*Present address: Solid State Physics Group, Tata Institute for Fundamental Research, Homi Bhabha Road, Bombay 400005, India.

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