Specific heat of YbBe$_{13}$

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We have measured the specific heat of single-crystal YbBe$_{13}$ from 0.4 to 25 K and compared it to Schottky anomalies based on two different previously reported Yb^{3+} crystal-field spectra. Qualitative agreement is found with the level scheme determined by inelastic neutron scattering, and small quantitative discrepancies are consistent with a strongly enhanced electronic contribution ($\gamma \sim 30$ mJ/mole K^2). T_N is determined to be 1.115 ± 0.016 K.

INTRODUCTION

YbBe$_{13}$ (Ref. 1) has been the subject of a number of recent studies which have focused on the question of a possible valence instability in the $4f$ shell of the Yb^{3+} ion. Magnetic susceptibility,[2] EPR,[2] and Mössbauer[3] and inelastic neutron scattering spectra[4] have been measured, each yielding conflicting results concerning the ordering and separation of the crystal-field (CF) levels within the ground-level term in Yb^{3+}. In particular, the susceptibility measurements yield a Γ_7 ground state with the Γ_6 and Γ_8 multiplets lying above it by $19k_B$ and $46k_B$, respectively. In contrast, the neutron scattering data give a Γ_7 ground state, but with the Γ_6 and Γ_8 levels lying above it by $51.0k_B$ and $37.2k_B$, respectively, i.e., reversed compared to the susceptibility results. In addition, there is anomalous broadening of the neutron scattering quasielastic line, which the authors attribute to a hybridization of the $4f$ and $5d$ electrons. We now have measured the specific heat of this compound to shed light on the CF level arrangement and to see whether the proposed interactions could be observed in the low-lying excitations of the conduction-electron system.

SAMPLE AND EXPERIMENTAL

The sample used in the present measurement was a single crystal, weighing 120 mg, and was grown from Al flux. Since the present work is the first of a series of low-temperature specific-heat measurements on metallic magnetic systems, we will briefly describe the calorimeter. The measurements were performed with a standard adiabatic heat-pulse method. The sample holder consisted of a sapphire substrate, supported by cotton threads, with a thin Au film deposited on the underside, serving as a heater. The thermometer was a small (2—3 mm) chunk of the graphite core of a Speer 220-Ω resistor, supported in a strainless configuration, and Manganin leads were affixed with silver epoxy. Thermal conduction between the sample and holder was obtained with Apiezon-N grease. The heat capacity of the sample holder was measured separately and at 20 K constituted roughly 6% of the total. The vacuum can surrounding the calorimeter assembly was designed to fit in the bore of a superconducting magnet, and is part of an Oxford Instruments top-loading ^{3}He cryostat.

The thermometer was calibrated against a Lake Shore Cryotronics calibrated Ge resistor immediately after the data were obtained and before warming the calorimeter to room temperature. All four-wire resistances above 1.2 K were measured with a Quantum Design ac resistance bridge. Below 1.2 K a lock-in amplifier was used to measure the resistance of the sample thermometer.

DISCUSSION

The specific heat of YbBe$_{13}$ from 0.4 to 25 K is shown in Fig. 1. The dominant features are the expected peak due to ordering of the ground-state doublet near 1 K, and the broad CF Schottky peak at higher temperature. In Fig. 2 we show the measured entropy and compare it to the Schottky anomalies using CF level schemes based on susceptibility[2] ($W = 1.9k_B$, $x = 0.45$) and inelastic neutron scattering[4] ($W = 1.79k_B$, $x = 0.911$) studies (W and x are the standard CF level parameters for f-electron
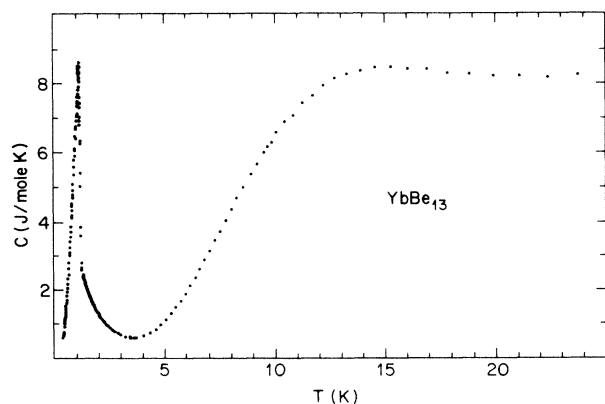
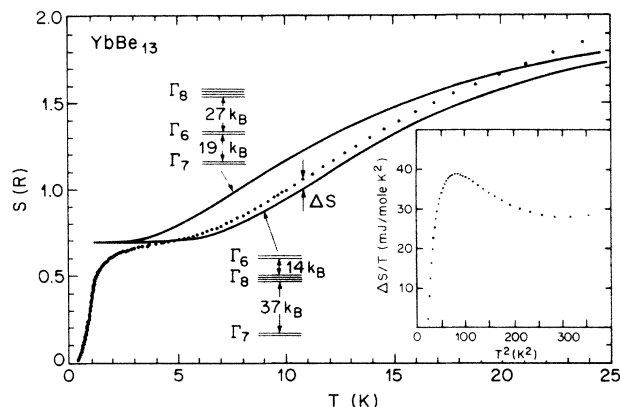FIG. 1. Specific heat of YbBe$_{13}$ from 0.4 to 25 K.

FIG. 2. Entropy of $YbBe_{13}$ from 0.4 to 25 K. The two solid lines are calculated using the two crystal-field level schemes discussed in the text. The inset shows the difference divided by T, between the observed entropy and the lower curve, indicating an electronic specific heat γ of order 30 mJ/mole K^2.

FIG. 3. Specific heat and entropy (inset) of $YbBe_{13}$ in the neighborhood of the antiferromagnetic phase transition at 1.1 K.

terms[5]). It is clear that better agreement is obtained with the neutron scattering results, and that this simple level scheme, described above, predicts the gross behavior quite well. In Fig. 3 we show the specific heat and entropy developed at the antiferromagnetic transition. We find $T_N = 1.115 \pm 0.016$ K, which is in conflict with the reported[2] T_N of 1.28 K, but probably not in conflict with the actual data in Ref. 2 since it is claimed that the susceptibility actually peaks at 1.28 K, instead of going through an inflection point, which is the usual signature of an antiferromagnetic phase transition.

The moderate discrepancy between the calculated Schottky anomaly based on the neutron scattering CF level parameters and our data is a source of concern. The error limits in the neutron results are small and, hence, are not suspect. In our measurement, the main sources of error in the entropy arise from the lattice contribution correction and the correction for the entropy developed below 0.4 K. For the lattice contribution we used the published values for the specific heat of the nonmagnetic isomorph $LuBe_{13}$.[1] This amounts to 1.3% of the total entropy at 20 K. In order to estimate the entropy developed below our lowest datum point at ~ 0.4 K, we used a T^3 law, appropriate for the specific heat of antiferromagnetic three-dimensional magnons. This amounts to an additive correction of $0.025R$, which is only 1.7% of the total at 20 K. Both of these corrections are small, and therefore the uncertainty due to each should be negligible. We are forced therefore to consider alternative explanations of the observed entropy difference.

It is quite possible that the observed discrepancy is somehow related to the anomalous broadening of the neutron scattering quasielastic line. If this is the case, then the interaction between the local spins and the conduction electrons might be significant, allowing the latter to re-
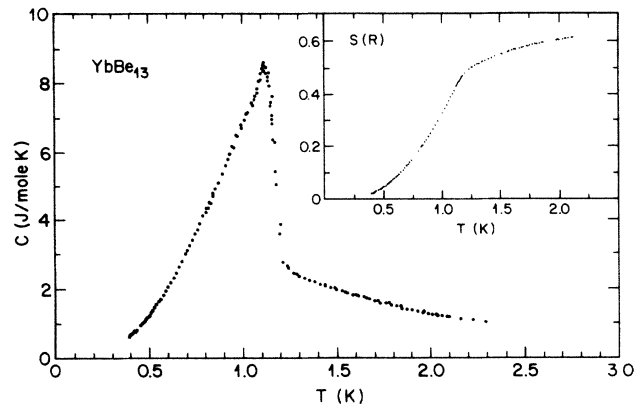
move local moment entropy with a different temperature dependence than that expected from a Schottky anomaly. To clarify this idea, we plot the difference entropy, divided by T in the inset of Fig. 2. We see that the behavior over most of the measured range is that of a linear term with a specific-heat coefficient $\gamma \sim 30$ mJ/mole K^2. The eventual ordering of the ground doublet causes the sharp decrease below 5 K, and the broad upturn near 10 K is most likely due to electron scattering from short-range fluctuations which accompany the transition to antiferromagnetic order. This proposed γ for $YbBe_{13}$ should be compared to the corresponding value $\gamma \sim 0.6$ mJ/mole K^2 reported[1] for $LuBe_{13}$. This is a significant difference and suggests the presence of a strong exchange interaction between the fluctuating local Yb^{3+} spins and the conduction electrons. This point is supported qualitatively by the anomalous, large quasielastic linewidth and the proposed explanation in terms of hybridization of $4f$ and $5d$ electrons.

In conclusion, we have measured the specific heat of $YbBe_{13}$ and have found good agreement with the neutron scattering CF level scheme. The agreement is improved by interpreting the small difference between the measured and neutron scattering derived entropy as a linear term due to electrons with a large effective mass. The mechanism which generates this large mass might also be responsible for the anomalous quasielastic line broadening. The low-temperature thermal behavior is dominated, however, by the localized $4f$ electrons of the Yb^{3+} ion subject to a crystal field, and the ground-state doublet orders in an antiferromagnetic transition at 1.1 K.

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