Nuclear Schottky effect in thulium

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The nuclear contribution to the specific heat of thulium has been investigated in the temperature range 0.02–0.6 K and in the presence of a magnetic field. The data can be well fitted to $C=\gamma T+\alpha T^3+C_N$, where the first two terms represent the electronic and the lattice contribution, respectively, and C_N is the nuclear specific heat. Using a two-level Schottky model for C_N, a ground-state energy splitting of 8.2×10^{-6} eV and a degeneracy ratio of 1.28 were calculated. Consistent with the estimated very large effective magnetic field (565 T), an external magnetic field up to 14 T was found to have no significant effect on C_N.

Below 1 K, the specific heat of thulium and other rare earths presents a large anomaly due to the magnetic hyperfine interaction between the unpaired $4f$ electrons and the magnetic moment of the nucleus. In the presence of the unfilled $4f$ orbitals a strong magnetic field is generated at the nucleus. This field produces the splitting of the nuclear spin states. While at high temperature the distribution of these states is uniform with a random orientation of the nuclear spins, at low temperature the lower energy spin states is preferred. The change in entropy associated to the change in population of these levels leads to a peak in the specific heat C. The overall C vs temperature T curve has the typical shape of a Schottky curve with a peak situated in the temperature range corresponding to the splitting energy gap.

Previous specific heat measurements performed on various rare-earth metals showed an increase in the specific heat below 1 K, which was attributed to a Schottky effect associated to the hyperfine splitting.[1–11] However, in most cases the Schottky peak occurs at such a low temperature that only the high-temperature side of the anomaly in the $C(T)$ curve was observed.

The splitting energy gap, which is of fundamental interest, cannot be obtained from the high-temperature data only since the high-temperature dependence of the nuclear specific heat behaves as $C_N\approx aT^{-2}$, where a depends on both the energy gap and the degeneracy of the energy levels. On the other hand, the analysis of the full curve, including its maximum, allows the independent determination of both the energy gap *and* the degeneracy ratio.

We report here a measurement of the specific heat of thulium metal in the temperature range 0.02–0.6 K. We show that the data can be expressed as $C=\gamma T+\alpha T^3+C_N$, where the first two terms represent, respectively, the electronic and the lattice specific heat. We also show that a good fit for C_N may be obtained using a two-level classical Schottky model.[12] Values for the splitting energy gap, the effective magnetic field, and the degeneracy ratio are also obtained.

The measurements were performed in a ^{3}He/^{4}He dilution refrigerator, using a relaxation time method.[13] The thulium was purchased from Goodfellow Company (Cambridge, England) under the form of a 0.1-mm thick foil of 99.9% purity. From this foil we cut a sample of 2.4 mg. We have used such a small sample mass in order to reduce the internal relaxation time (i.e., the diffusivity of the sample). We used a RuO_2 resistor as temperature sensor. The sensor was previously calibrated at zero magnetic field (B) and up to $B=14$ T. For the calibration a good fit has been obtained using the following relation:

$$\ln T=\sum_{n=0}^{3}A_n(\ln R)^n\ . \tag{1}$$

As a heater, we used a 120-Ω strain gauge purchased from Tokyo Sokki Kenkyujo Co. The addenda heat capacity, was determined in a previous experiment, and represents less than 0.1% of the sample heat capacity at any temperature.

The heater and the temperature sensor were attached to the opposite sides of the sample with a very small amount of GE 7032 low-temperature varnish. The electrical contacts to the heater and the thermometer, which also serve as mechanical support, were realized using 60-μm NbTi wires. A 60-μm copper wire was added in order to increase the thermal link between the sample and the copper cold finger.

Data were obtained from the analysis of T vs time during the relaxation period, resulting from the application of a heat pulse which increased the initial sample temperature by $\approx10\%$. In that case, the error due to the finite size of the temperature step is kept below 0.2%, much less than the error due to the thermometry ($\approx2\%$).

The experimental specific heat data are presented in Fig. 1 together with higher-temperature data obtained by Lounasmaa.[1] A good agreement is found between Lounasmaa's results and ours in the temperature range where overlap exists.

The solid curve presented in Fig. 1 corresponds to the best fit of the data to

$$C=\gamma T+\alpha T^3+C_N\ . \tag{2}$$

For C_N, we used a two-level Schottky model according

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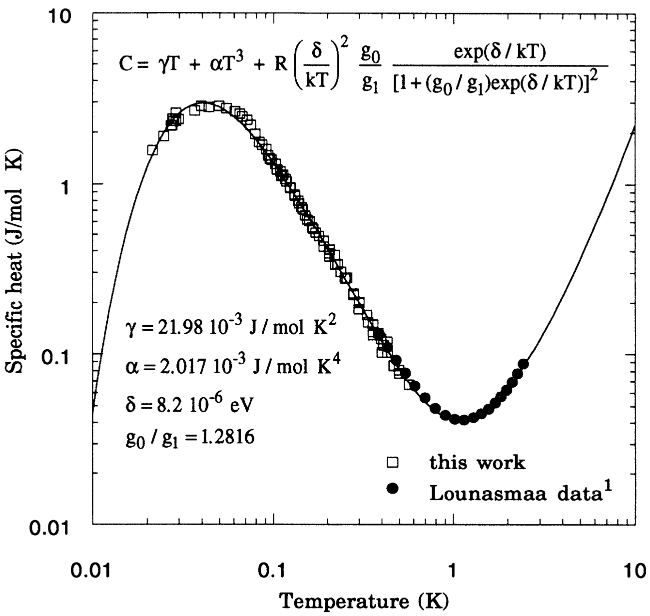

FIG. 1. Temperature dependence of the specific heat of Tm metal. The fit represents the sum of the three contributions to the specific heat: electronic, lattice, and nuclear specific heat, respectively.

to the fact that the stable thulium isotope Tm^{169} has only two nuclear energy levels $i=+\frac{1}{2}$ and $i=-\frac{1}{2}$ in the ground state. In that case, the nuclear Schottky specific heat is given by

$$C=\gamma T+\alpha T^3+R\left[\frac{\delta}{kT}\right]^2\frac{g_0}{g_1}\frac{\exp(\delta/kT)}{[1+(g_0/g_1)\exp(\delta/kT)]^2}\ , \tag{3}$$

where $R=8.314$ J/mol K is the molar gas constant, δ is the splitting energy gap, k is the Boltzmann constant, and g_0, g_1 represent the degeneracies of the two levels.[12]

Fitting the data with Eqs. (2) and (3), we obtain $\gamma=22\times10^{-3}$ J/mol K^2, $\alpha=2\times10^{-3}$ J/mol K^4, a degeneracy ratio $g_0/g_1=1.28$, and an energy separation $\delta=8.2\times10^{-6}$ eV or $\delta/k=0.095$ K. The splitting energy is in good agreement with Mössbauer experiment results that give $\delta=9.04\times10^{-6}$ eV.[14]

The remarkably good agreement between the data and the two-level Schottky model clearly indicates the absence of a quadrupolar effect which would strongly affect the shape of the Schottky curve.[8] Indeed, since there are only two energy levels ($i=+\frac{1}{2}$ and $i=-\frac{1}{2}$) for thulium, no quadrupole interactions are expected,[1] which is in agreement with our observation. It is also clear that, in the temperature range investigated, no sign of a second-order effect, due to the influence of next neighboring atoms, is observed.

Within the experimental error of a few percent, no effect of an external magnetic field on the specific heat was observed. In the framework of the hyperfine splitting theory, one defines an effective magnetic field:

$$B_{\text{eff}}=\frac{\delta I}{\mu}\ , \tag{4}$$

where $\mu=0.229\mu_N$ is the nuclear magnetic moment of thulium, μ_N is the nuclear magneton, and for thulium $I=\frac{1}{2}$.[14–16] This field induces the splitting of the nuclear energy levels, and an external magnetic field is expected to interact with the nucleus and change the splitting energy. If the external magnetic field is large enough compared to B_{eff} the nuclear Schottky specific heat is affected, as recently demonstrated in Co-based granular solids.[17] In our case, $B_{\text{eff}}=565$ T and the specific heat remains unchanged up to $B=14$ T.

In the present work, we reported a low-temperature specific heat measurement of thulium metal. A large anomaly is observed in the specific heat behavior with a peak around 0.04 K. This anomaly is attributed to a nuclear Schottky effect produced by the splitting of the nuclear ground state in the presence of a very important effective magnetic field ($B_{\text{eff}}\approx565$ T) produced by the unpaired $4f$ electrons. The splitting energy is estimated to be 8.2×10^{-6} eV and the degeneracy ratio to be 1.28. A good agreement is found with previous higher-temperature specific-heat data and Mössbauer experiments, and with statistical-mechanics theory. No significant effect of the external magnetic field has been observed in the range 0–14 T, consistent with the very large effective field of thulium.

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