Magnetic-field dependence of Schottky specific heat in the 1/1 Zn-Sc-Tm approximant

J Dolinšek

J. Stefan Institute and University of Ljubljana, Faculty of Mathematics and Physics, Jamova 39, SI-1000 Ljubljana, Slovenia

E-mail: jani.dolinsek@ijs.si

Abstract. The analysis of low-temperature specific heat of rare-earth (RE)-containing quasicrystals and periodic approximants and consequent interpretation of their electronic properties in the $T \to 0$ limit is frequently hampered by the Schottky effect, where crystalline electric fields lift degeneracy of the RE-ion Hund's rule ground state and introduce additional contribution to the specific heat. When the low-temperature specific heat C is analyzed in the C/T versus T^2 scale, the Schottky effect (a single-ion property in a system of non-interacting electrons) and the electron-electron interactions both yield a very similar upturn in the $T \to 0$ limit. The origin of the upturn can be unraveled from the magnetic-field dependence of the low-temperature specific heat.

1. Introduction

When studying electronic properties of rare-earth (RE) containing quasicrystals and their approximants from the low-temperature specific heat, there is a drawback which often hampers the interpretation of experimental data, namely the crystal-field (CF) splitting of the Hund's rule ground state [1]. The highly anisotropic 4f charge cloud of a RE ion (with the exception of the spherically symmetric gadolinium) interacts with the crystalline electric field and lifts the $(2J + 1)-$fold degeneracy of its ground state with the total angular momentum $\hbar \vec{J}$, producing a set of discrete energy levels. Specific heat of a system with discrete energy levels possesses an additional contribution that becomes dominant at low temperatures, known as the Schottky effect [2]. The Schottky specific heat C_{Sch} is characterized by a broad peak, appearing at a temperature that is a fraction of the energy difference $\Delta\varepsilon/k_B$ (in temperature units) between the CF-split energy levels. For small CF splittings, the peak may appear in the Kelvin- or sub-Kelvin temperature range, where it obscures the electronic specific heat. Precise determination of the electronic specific heat coefficient may thus be difficult and uncertain for quasicrystals containing RE elements. In addition, when the low-temperature total specific heat is presented in a C/T versus T^2 scale (as it is customary done), the Schottky specific heat term yields an upturn in the $T \to 0$ limit that cannot be easily distinguished from a similar upturn produced by the electron-electron interactions in exchange-enhanced systems and strongly correlated systems. The low-temperature magnetic susceptibility can also be affected by the CF effects [1,3,4]. The CF-split energy level scheme of some RE ions contains a non-magnetic ground state, whereas higher levels are magnetic. In the $T \to 0$ limit, the weight of the non-magnetic state in the electronic magnetization increases, so that the magnetic susceptibility χ decreases, resulting in a Curie-Weiss-like deviation from the linear $\chi^{-1} \propto T$ Curie behavior. However, both the CF-induced Curie-Weiss

behavior of the susceptibility and the Schottky specific heat are single-ion properties, depending on the distribution of electric charges around the RE ion, but are not related to the interactions within the electronic system.

In a recent publication [5] we have demonstrated the existence of Schottky effect in the i-Zn-Ag-Sc-Tm Tsai-type icosahedral quasicrystal (i-QC) and its Zn-Sc-Tm 1/1 cubic approximant. We have first derived the CF Hamiltonian pertinent to the class of Tsai-type i-QCs and their approximants, which includes most of the known RE-containing quasicrystalline systems. In the Tsai-type atomic clusters, the RE elements are located on fivefold axes of a three-shell icosahedral atomic cluster that represents the backbone of the structure, so we have derived the CF Hamiltonian for the pentagonal (5-fold) rotational symmetry of the crystalline electric field. Using the leading term of this Hamiltonian, we have calculated analytically the Schottky specific heat in the presence of an external magnetic field and made comparison to the experimental specific heat of the i-$Zn_{74.5}Ag_{9.5}Sc_{12}Tm_4$ i-QC (abbreviated as i-Zn-Ag-Sc-Tm) and its 1/1 bcc approximant $Zn_{85.5}Sc_{11}Tm_{3.5}$ (abbreviated as 1/1 Zn-Sc-Tm). In these systems, the CF-split energy levels of thulium ions introduce Schottky contribution to the specific heat that exhibits a broad maximum at a temperature around 1 K and the maximum is shifted to higher temperatures by the application of an external magnetic field. We have also shown that even the nuclear Schottky effect, being much smaller effect than the ionic Schottky effect, is experimentally observed in the specific heat.

2. The low-temperature specific heat

The low-temperature specific heat of a RE-containing metallic alloy in the paramagnetic phase is a sum of the electronic, lattice and Schottky contributions [2], $C = \gamma T + \beta_3 T^3 + C_{Sch}$, where γ and β_3 are the electronic and lattice specific heat coefficients, respectively, and C_{Sch} is the Schottky specific heat. When analyzing the low-temperature specific heat in a C/T versus T^2 scale, one obtains for non-magnetic alloys in the absence of the Schottky contribution ($C_{Sch} = 0$) a straight line $C/T = \gamma + \beta_3 T^2$. In the presence of the Schottky contribution, the specific heat data presented in this scale show a low-temperature upturn. This is demonstrated in Fig. 1 on the example of the 1/1 Zn-Sc-Tm approximant, where the zero-field specific heat is shown in such kind of a plot. In metallic systems with incompletely filled d or f shells, electron-electron exchange interactions may provide another term to the specific heat that also produces a low-temperature upturn in the C/T versus T^2 scale. Such systems are known as the exchange-enhanced systems [6] and show instability to magnetism, i.e., they are close to a phase transition between a paramagnetic and a magnetically ordered phase. The interacting electrons give rise to long-lived spin fluctuations (similar to spin waves), which in the quantized form are called paramagnons or virtual magnons. The interaction of the electrons with paramagnons gives rise to an enhanced effective mass of the electrons (manifested in an increased γ value) and a logarithmic term in the electronic specific heat at low temperatures, which can be represented by a general equation of the form [6]

$$C = \gamma T + AT^3\ln(T/T_{sf}) + \beta_3 T^3, \tag{1}$$

where T_{sf} is the spin fluctuation temperature. The logarithmic term is negative for $T < T_{sf}$, so that the total specific heat shows an upturn at low temperatures when plotted as C/T versus T^2. The logarithmic term in the electronic specific heat was derived also without invoking the idea of paramagnons; it was found in ^{3}He due to temperature-dependent interparticle interaction [7], suggesting that the $T^3\ln T$ behavior of the low-temperature specific heat may be a general feature of Fermi-liquid systems.

3. Results and Conclusions

In order to demonstrate the difficulty of distinguishing between the Schottky effect and the electron-electron interactions when analyzing the low-temperature upturn in the specific heat, we present in Fig. 1 the fit of the zero-field specific heat data of the 1/1 Zn-Sc-Tm "Schottky" system with the Eq. (1) rewritten in the form $C/T = \gamma + AT^2\ln(T/T_{sf})$, valid for an exchange-enhanced system. The fit

is shown by a solid curve (the fit parameters are given in the Figure caption), where it is seen that the logarithmic term reproduces excellently the low-temperature upturn due to the Schottky effect in a limited temperature interval. The low-temperature upturn can also be reproduced qualitatively by a power-law function of a form $C/T = BT^{-n}$ (with $n > 0$), as used in the study of quantum critical phenomena arising from strongly correlated 4f electrons in Fermi-liquid systems, where the zero-field C/T diverges as a power law in the $T \to 0$ limit. The fit of the 1/1 Zn-Sc-Tm C/T data with the power-law function is shown in Fig. 1 as a dashed curve (the fit parameters are given in the Figure caption), where it is evident that it qualitatively reproduces the low-temperature upturn. The analysis of the low-temperature specific heat of RE-containing quasicrystals and approximants may thus be ambiguous, as the Schottky effect and the electron-electron interactions both yield a very similar upturn in the C/T versus T^2 scale.
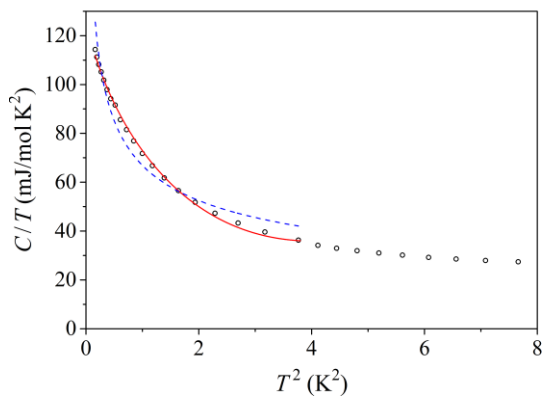

Figure 1. Low-temperature zero-field specific heat of the 1/1 Zn-Sc-Tm "Schottky" system in a C/T versus T^2 scale. Solid curve is the fit with $C/T = \gamma + AT^2\ln(T/T_{sf})$, valid for an exchange-enhanced system (the fit parameters of the curve are $\gamma = 127.7$ mJ/mol·K^2, $A = 46$ mJ/mol·K^4, and $T_{sf} = 3.3$ K). Dashed curve is the fit with a power-law function $C/T = BT^{-n}$ (the fit parameters of the curve are $B = 66.9$ mJ/mol·K^2 (where the temperature is considered to be dimensionless) and $n = 0.7$).
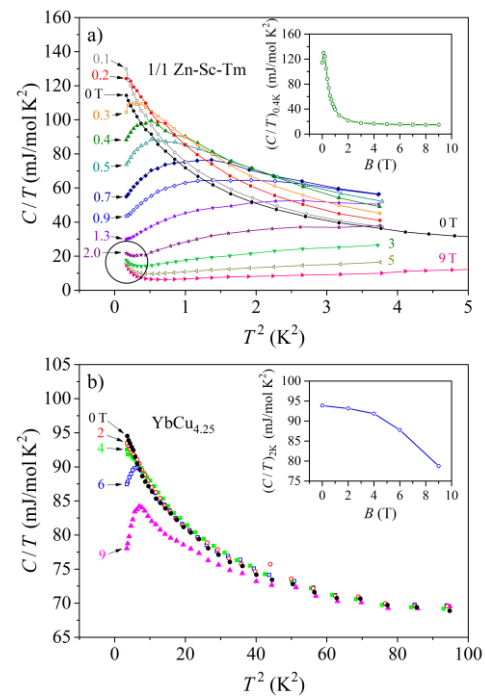

Figure 2. (a) Low-temperature specific heat of the 1/1 Zn-Sc-Tm. The upturn due to the nuclear Schottky effect is encircled. The inset shows $(C/T)_{0.4K}$ as a function of B. **(b)** Low-temperature specific heat of the YbCu$_{4.25}$ heavy-fermion compound. The inset shows $(C/T)_{2K}$ as a function of the magnetic field.

The origin of the upturn can be unraveled from the magnetic-field dependence of the low-temperature specific heat, where the Schottky effect (a single-ion property in a system of non-interacting electrons) and the electron-electron interactions in an exchange-enhanced system yield different behavior. This is demonstrated experimentally by comparing the field-dependent specific heats of the 1/1 Zn-Sc-Tm approximant and the YbCu$_{4.25}$ heavy-fermion compound, belonging to the class of strongly correlated systems. In Fig. 2, the specific heat of the 1/1 Zn-Sc-Tm "Schottky" system in the temperature interval between 0.4 and 2 K at different magnetic fields is shown in a C/T versus T^2 scale. The zero-field specific heat and the specific heat in the lowest applied field of 0.1 T show the same shape of the $T \to 0$ upturn, but the 0.1-T curve lies higher than the zero-field curve in the entire presented temperature range. The specific heat in the next higher field of 0.2 T is also larger than the zero-field

specific heat, but the shape of the upturn starts to change with a tendency to round at the lowest temperature. For the fields above 0.2 T, the upturn evolves into a maximum, which moves to higher temperatures with an increasing field (a property of the Schottky maximum). The specific heat curves in the field $B \geq 0.3$ T cross the zero-field curve at some temperature, lying below the zero-field curve in the low-temperature limit and becoming higher at elevated temperatures. The Schottky maximum with its characteristic dependence on the magnetic field is thus well observed also in the C/T versus T^2 scale. In addition, the low-temperature upturn due to the nuclear Schottky effect also becomes observed in the specific heat curves at fields above 2 T (shown encircled in Fig. 2). Since the ^{169}Tm nuclei (of 100 % natural abundance) possess spin $I = 1/2$, the nuclear quadrupole interaction is zero and the nuclear Schottky effect originates from the Zeeman interaction with the effective magnetic field. Another convenient way of demonstrating the motion of the Schottky maximum with the magnetic field to higher temperatures is to plot the C/T value at the lowest investigated temperature (0.4 K in our case) as a function of the magnetic field. This is presented in the inset of Fig. 2, where the $(C/T)_{0.4K}$ value first increases with the magnetic field, passes through a maximum and then decreases at higher fields, following the field-induced shift of the Schottky maximum to higher temperatures. The asymptotic $(C/T)_{0.4K}$ value reached in the high-field limit is close to zero and is determined by the nuclear Schottky specific heat. The magnetic-field dependence of the low-temperature specific heat of an exchange-enhanced system is different, as will be illustrated on the example of the YbCu$_{4.25}$ heavy-fermion (HF) compound [8]. YbCu$_{4.25}$ is a giant-unit-cell complex intermetallic, which was reported to be a "moderate" HF compound with the increase of the thermal effective mass of the charge carriers by a factor of 84.5 with respect to the free-electron mass. The low-temperature specific heat of the YbCu$_{4.25}$ in magnetic fields between zero and 9 T is shown in Fig. 2 in a C/T versus T^2 scale. The zero-field specific heat shows a $T^3\ln T$ logarithmic upturn, present in this compound due to the strong exchange interactions between the Yb f-electrons and the conduction electrons. In a magnetic field, the specific heat at low temperatures is lowered with respect to the zero-field curve for any field value, and the decrease is stronger in higher fields. In addition, a high-enough magnetic field (above 6 T in this case) introduces sharp maximum in the C/T curve at a temperature, which depends weakly on the magnetic field. When plotting the $(C/T)_{2K}$ value (2 K was the lowest investigated temperature) as a function of the magnetic field (inset in Fig. 2), the curve does not exhibit a maximum as in the case of the Schottky effect, but decreases monotonously with the field. The field-induced decrease of the $(C/T)_{2K}$ value is relatively small; in the 9-T field it has dropped only by 17 % with respect to the zero-field value (note the highly expanded vertical scale in the inset of Fig. 2). This behavior is typical for HF systems, where it originates from the fact that the external magnetic field gradually destroys the Kondo-type compensation of the f-electron magnetic moments by the oppositely spin-polarized conduction-electron cloud that builds up around the RE ion, making the f-electron moments to reappear in the field. Therefore, careful inspection of the low-temperature specific heat behavior in a magnetic field is crucial to distinguish whether the upturn originates from the Schottky effect or it is due to the electron-electron interactions in an exchange-enhanced system.

References

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