The semimetallic $S = 1/2$ antiferromagnetic chain Yb_4As_3: quantum transfer-matrix simulations and experimental field-dependent specific-heat data

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The $S = 1/2$ antiferromagnetic Heisenberg model with the Dzyaloshinsky–Moriya interaction is applied to Yb_4As_3. In this paper we calculate the specific heat of this model, mapped onto the isotropic Heisenberg model with both uniform field B^x and staggered field B_s^y, by the numerical quantum transfer-matrix (QTM) method and we present new experimental results for the polydomain sample in the applied field.

1 Introduction

One-dimensional systems have attracted the interest of chemists and physicists for more than three decades. The theory of the ideal uniform $S = 1/2$ antiferromagnetic Heisenberg chain in the magnetic field is well established and usually well describes the observed properties in real systems. The majority of these systems are organic and inorganic compounds with chains of $3d$ and $4f$ ions. Recently, a new class of rare-earth pnictide compounds like Yb_4As_3 have become the focus of attention.

The Yb_4As_3 is a pnictide compound which belongs to a family of R_4X_3 (R = rare-earth, X = As, Bi, P, Sb) compounds of the anti-Th_3P_4 structure. At high temperatures (above $T_{co} \approx 295$ [K]) Yb_4As_3 is a homogeneous intermediate valent (IV) metal with a valence ratio of $Yb^{2+}/Yb^{3+} = 3:1$ [1]. The Yb-ions occupy the Phosphorus sites at the three-fold symmetry axes, the As-ions are located at the Thorium sites. The Yb-sites can be viewed as being aligned along four families of interpenetrating chains oriented parallel to the space diagonals of a cube, known as body-centered cubic rod packing [2]. At $T_{co} \approx 295$ [K] the IV state exhibits a charge-ordering instability such that far below T_{co} one of the four Yb ions becomes trivalent and forms a one-dimensional spin $S = 1/2$ chain along the $[111]$ direction [3]. At low temperatures, Yb_4As_3 is semimetallic with extremely low carrier concentration of 10^{-3} As-$4p$ holes per formular unit [4]. The Yb^{3+} ion has one hole in the $4f$ closed shell. The $J = 7/2$ ground multiplet splits into four doublets as a result of the crystalline field effect. Thus the

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low-temperature dynamics is described by an effective $S = 1/2$ spin chain. The neutron scattering experiments on Yb_4As_3 actually confirmed that the excitation spectrum is well described by the one-dimensional $S = 1/2$ isotropic Heisenberg model [5] in the absence of magnetic field. The interchain interactions are small and ferromagnetic, leading to a low-T spin-glass freezing [2].

Although the system in low-temperatures and in the absence of a magnetic field exhibits a typical heavy-fermion behavior with linear specific heat coefficient $\gamma \approx 200$ mJ/(K^{2}mol), finally it has been attributed to 1D spin excitations in the Yb^{3+} chains [2, 3]. Moreover, under magnetic field, the gap in the spin excitation spectrum of Yb_4As_3 opens and fulfils the power low $H^{2/3}$ [6] which gives the strong experimental evidence for the existence of a staggered field alternating along the Yb^{3+} chains induced by the Dzyaloshinsky–Moriya interaction.

In the present paper, neglecting the interchain coupling, we calculate the field-dependent specific heat of Yb_4As_3 in a wide range of temperatures (above 4 K, where uncertainties of our extrapolations are below 3%), using the Heisenberg model with the Dzyaloshinsky–Moriya interaction [2, 7]. We would like to check if the experimental specific heat data obtained for a polydomain sample of the compound studies can be accounted for within this model. An alternative model with intrachain dipolar interactions [8] or the sine-Gordon model [9] should also be considered.

2 Theoretical approach and results

To characterize the finite-temperature properties of the Yb_4As_3, we consider the $S = 1/2$ anisotropic Heisenberg model with the Dzyaloshinsky–Moriya interaction [7]. The Dzyaloshinsky–Moriya interaction can be eliminated by rotating the spins in the x-y plane by the angle θ [7]. Then the model is mapped onto [7]

$$\mathcal{H} = -\left\{ J \sum_{i=1}^{N} (S_i^x S_{i+1}^x + S_i^y S_{i+1}^y + S_i^z S_{i+1}^z) + g_\perp \mu_B B^x \sum_{i=1}^{N} S_i^x + g_\perp \mu_B B_s^y \sum_{i=1}^{N} (-1)^i S_i^y \right\}, \tag{1}$$

where $B^x = B\cos(\theta)$, $B_s^y = B\sin(\theta)$ and B is the uniform external magnetic field perpendicular to the one-dimensional spin-chain. Equation (1) describes the effective isotropic Heisenberg model with both the uniform field B^x and the transverse staggered field B_s^y.

We express Hamiltonian (1) as a sum $\sum_{i=1}^{N} \mathcal{H}_{i,i+1}$ of the spin-pair operators $\mathcal{H}_{i,i+1}$, where

$$\mathcal{H}_{i,i+1} = -\{J\,\mathcal{S}_i \cdot \mathcal{S}_{i+1} + \tfrac{1}{2} g_\perp \mu_B [B^x (S_i^x + S_{i+1}^x) + (-1)^i B_s^y (S_i^y - S_{i+1}^y)]\}\,. \tag{2}$$

In the checker-board decomposition we divide the Hamiltonian (1) into two non-commuting parts $\mathcal{H} = \mathcal{H}^{\text{odd}} + \mathcal{H}^{\text{even}}$, each part defined by the commuting spin-pair operators $H_{i,i+1}$. Then the series of the classical approximants of the quantum thermal values can be found, using the general Suzuki–Trotter formula. The partition function $\mathcal{Z}$ is calculated from the approximant

$$\mathcal{Z}_m = \mathrm{Tr}\left[\prod_{r=1}^{m} \mathcal{V}_{2r-1,2r} \prod_{r=1}^{m} \mathcal{V}_{2r,2r+1} \right]^{N/2}, \tag{3}$$

in the limit $m \to \infty$, where $\mathcal{V}_{r,r+1}$ is the local transfer matrix.

To perform the trace operation, we define a unitary shift operator $\mathcal{D}$

$$\mathcal{D} \equiv \sum_{s_1^z} \cdots \sum_{s_{2m}^z} |s_3^z \ldots s_{2m}^z s_1^z s_2^z\rangle \, \langle s_1^z s_2^z s_3^z \ldots s_{2m}^z| \,, \tag{4}$$

where s_i^z is the eigenvalue of the z component of the spin operator $\mathcal{S}_i$. Using Eq. (4), we can express the operators $\mathcal{V}_{r,r+1}$ ($r = 1, 2, \ldots, 2m$) in terms of the operators $\mathcal{V}_{1,2}$ and $\mathcal{V}_{2,3}$ so that the m-th classical approximant of the partition function amounts to

$$\mathcal{Z}_m = \mathrm{Tr}(\mathcal{W}_1 \mathcal{W}_2)^{N/2}\,, \tag{5}$$

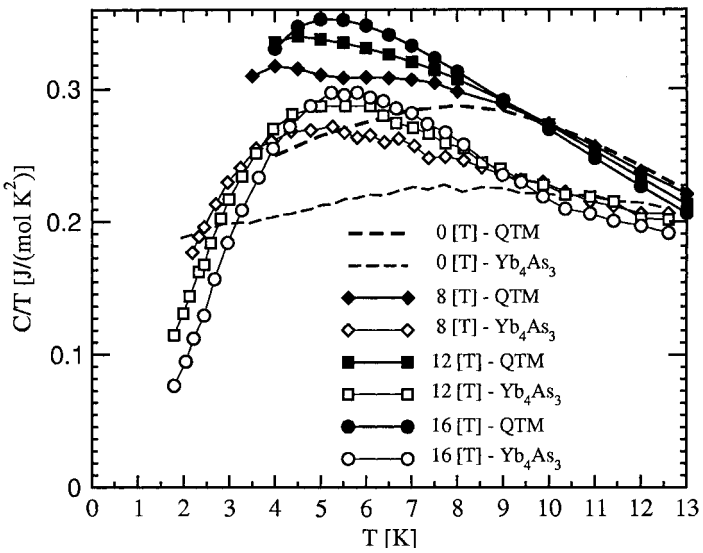

Fig. 1 Comparison of the measured specific heat after phonon subtraction and QTM calculation for Yb_4As_3. The dashed curves represent zero-field specific heat and remaining symbols represent specific heat for various finite magnetic fields.

where

$$\mathcal{W}_r = \left(\mathcal{V}_{r,r+1}\mathcal{D}^+\right)^m, \qquad r = 1,2\,. \tag{6}$$

The numerical implementation of (5) is based on two global transfer operators $\mathcal{W}_r$ $(r = 1,2)$ expressed by the sparse matrices defined by the operators $\mathcal{V}_{r,r+1}$ $(r = 1,2)$. Moreover, in the limit $N \to \infty$ the partition function $\mathcal{Z}$ is equal the highest eigenvalue of the global transfet matrix $\mathcal{W} = \mathcal{W}_1\mathcal{W}_2$. The thermodynamic functions are related to the free energy $\mathcal{F} = -k_BT \ln \mathcal{Z}$ and the specific heat is given as its second derivative with respect to the temperature. We have performed the test numerical calculations of specific heat for $B_s^y = 0.01$ and a number of fields B^x and we have recovered the results of [7] given in Fig. 1.

In our simulations we adopt the parameters as they are known in literature. The g-factors parallel and perpendicular to the spin chain of Yb_4As_3 were estimated as of about $g_\parallel = 3.0$ and $g_\perp = 1.3$, respectively, from the analysis of the scattering vector dependence of the inelastic response at zero field and the induced moment on the Yb^{3+} ions measured by polarised neutron diffraction under magnetic field [6]. An intrachain exchange coupling ($J/k_B = -26$ [K]) [5] was found from the uniform susceptibility measurements. The magnetization measurements led to the value $\tan(\theta) = 0.19$ [7] so that the uniform field is about five times larger than the effective staggered field induced by the Dzyaloshinsky–Moriya interaction.

Using these microscopic parameters the quantum transfer-matrix simulations were applied to calculate the specific heat of the $S = 1/2$ spin chain both in the absence of the external magnetic field and in the finite external magnetic field perpendicular and parallel to the spin chain ($B = 4 - 20$ T). In high temperatures (above 7 K) we have performed our simulations for the Trotter number up to $m = 10$ and in low temperatures up to $m = 12$.

The specific heat results determined in the magnetic fields are presented in Fig. 1. The open symbols represent our experimental results for a polydomain sample with the magnetic field ($B = 8$ T, 12 T, 16 T) applied along the cubic [111] direction, and the filled symbols are numerical results. For the experimental data the phonon contribution $C_{\rm ph} = 2.05 \times 10^{-3}$ J/(K^{4}mol) $\cdot\, T^3$ has been subtracted [10]. The measurements were performed for a polydomain sample in which 25% of the domains were oriented with the spin chains parallel to the applied field B and about 75% of the domains were aligned so that the effective field component $B \times \sin(70^\circ)$ was perpendicular to the spin chains. With increasing magnetic field the molar specific heat maximum C/T increases, shifts to the right and crosses themselves at about 9 K which is consistent with the new experimental findings. However, our theoretical data systematically overestimate the experimental results. This might be related to imper-

fections in the charge-ordering [11] resulting in finite chains or to interchain coupling effects [12]. There is also some uncertainty in the experimental subtraction of the lattice contribution.

In conclusion, we have presented the field-dependent specific heat data and compared them with the quantum transfer-matrix calculations performed for the Heisenberg model with the Dzyaloshinsky–Moriya interactions, using the parameters found in literature, revealing the qualitative agreement with experiment.

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