Excitations in spin chains and specific-heat anomalies in Yb$_4$As$_3$

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Abstract. – An explanation is given for the observed magnetic-field dependence of the low-temperature specific-heat coefficient of Yb$_4$As$_3$. It is based on a recently developed model for that material which can explain the observed heavy-fermion behaviour. According to it, the Yb$^{3+}$ ions are positioned in a net of parallel chains with an effective spin coupling of the order of $J \approx 25$ K. The magnetic-field dependence can be understood by including a weak magnetic coupling $J'$ between adjacent chains. The data require a ratio $J'/J \approx 10^{-4}$. In that case the experimental results can be reproduced very well by the theory.

The low-carrier compound Yb$_4$As$_3$ which belongs to the rare-earth pnictide family has been subject of extensive experimental investigation caused by its intriguing low-temperature anomalies [1]-[9]. It shows evidence for a “heavy-fermion”–type behaviour below a characteristic temperature $T^* \approx 40$ K, notably a large $\gamma$-coefficient of about 200 mJ/mol · K$^2$ for the specific heat. On the other hand, the carrier concentration is extremely small, approximately $10^{-3}$ holes per formula unit below $T^*$. This excludes a conventional Kondo mechanism as the origin of the low-energy excitations leading to the large $\gamma$-value.

The scenario proposed in ref. [10] is quite different from that of a Kondo system. The crystal has the anti-Th$_3$P$_4$ structure, and the space group is $I43d$. The Yb ions occupy four systems of parallel chains oriented along the space diagonals of a cube (body-centred cubic rod packing) [11]. A structural phase transition at room temperature changes the high-temperature homogeneous mixed-valent state of Yb$_4$As$_3$ (Yb$^{3+}$ : Yb$^{2+}$ = 1 : 3) to a charge-ordered state where the 25% Yb$^{3+}$ holes are confined to one of the four chain systems, e.g., parallel ⟨111⟩-chains. The particular ordering of Yb$^{3+}$ ions was confirmed clearly by perturbed angular-correlation (PAC) measurements [6]. This state has almost half-filled hole bands which are subject to strong on-site Coulomb correlations, effectively described by a $t$-$J$ model. Therefore the low-energy excitations essential for the specific heat are the magnetic excitations of an antiferromagnetic quasi-one-dimensional “$S = \frac{1}{2}$” Heisenberg chain ($\mathbf{S}$ is the...
pseudospin corresponding to the lowest Kramers doublet of Yb$^{3+}$). This model proposed in ref. [10] was beautifully confirmed by the inelastic-neutron-scattering results of Kohgi et al. [7]. They show that low-temperature magnetic excitations in Yb$_4$As$_3$ are very well described by the one-dimensional spin-wave spectrum, $\omega(q) = (\pi/2)J \sin(aq)$, of des Cloizeaux and Pearson [12], where $q$ is the wave number in (111)-direction and $a$ the distance of Yb$^{3+}$ ions along the chain. More precisely, this dispersion describes the lower boundary of a continuum of spin excitations whose spectral function for a fixed momentum $q$ is strongly peaked at this lower boundary [13]. This also leads naturally to a linear specific heat for $k^* \sim J \ll 1$. From the maximum observed spin-wave energy of $3.8 \text{meV} \approx 40 \text{K}$ at $q = 1/2(\pi/a)$ one obtains $J = 25 \text{K}$ in good agreement with the energy scale $T^*$ estimated from the value of $\gamma$.

However, there is still one major challenge to the validity of the model proposed in ref. [10]. Concerning the dependence of $\gamma$ on an applied magnetic field $H$, one would expect deviations from $\gamma(H = 0)$ of the order $(H/J)^2$, i.e. about $10^{-2}$ at $4 \text{T}$ uniformly for all temperatures with $k_B T / J \ll 1$. Experiments by Helfrich et al. [2] revealed a quite different behaviour: Above $2 \text{K}$ changes in $\gamma$ are indeed small. In contrast, at $0.5 \text{K}$ the field dependence of $\gamma(H)$ is dramatic. Already at $4 \text{T}$ its value is strongly suppressed in conflict with the above argument. This indicates that an additional energy scale much smaller than $J$ (25 $\text{K}$) must be present in Yb$_4$As$_3$.

It is the purpose of this letter to show that the spin-chain model for Yb$_4$As$_3$ is well capable of explaining the unexpected results of Helfrich et al. For the present purpose we may neglect deviations from perfect charge ordering or half-filling which is only important for the transport properties. The additional energy scale which the results in ref. [2] suggest is associated with anisotropy gaps of the magnetic excitations caused by interchain coupling $J'$ of the parallel Yb$^{3+}$-spin chains. The complete excitation spectrum of a trigonal antiferromagnetically coupled chain system is calculated and it is shown how the linear specific-heat term and its field dependence arise. A comparison with the data of Helfrich et al. allows to estimate the magnitude of $J'$. Proposals for magnetic-resonance experiments are made.

It is well known that for a single chain, there cannot be any long-range spin ordering, but, according to calculations on the spin-1/2 Heisenberg chain [14], [15], the spin-spin correlation function decays slowly, $\langle S(r) \cdot S(0) \rangle \propto (-1)^r \sqrt{\log(r)}/r$, i.e. the correlation length is infinite. Our aim is a calculation of $\gamma(H)$ for the coupled-chain system which requires the excitation spectrum for all wave vectors and fields. For this purpose we have to resort to linear spin-wave approximation, i.e. we start from the appropriate broken-symmetry (Néel) state. We do not imply that Yb$_4$As$_3$ actually exhibits three-dimensional magnetic order, although this cannot be excluded at very low temperatures due to the effect of interchain coupling. In fact, the onset of a sharp specific-heat anomaly below $100 \text{mK}$ was observed [2], but no peak associated with the long-range order was found so far.

We transform the crystal coordinate system of the charge-ordered state to a new basis with a hexagonal unit cell where the (111)-direction now is oriented along the $c$-axis, i.e. it transforms to the (001)-direction. Taking into account the interchain coupling by a parameter $\Delta$, we describe Yb$_4$As$_3$ with a Hamiltonian of the form

$$ H = \sum_{\langle ij \rangle} \langle S_i \cdot S_j \rangle + dS_i^z S_j^z + \Delta \sum_{\langle ij \rangle} S_i \cdot S_j - h \sum_i S_i, $$

where $\Delta = J'/J$ is the ratio of the antiferromagnetic exchange constants perpendicular and parallel to the $c$-axis, and $h = g_\text{eff} \mu_B H / J$ is the applied magnetic field. All energies are in units of $J$. The dominant intrachain interaction is assumed to have a very small uniaxial anisotropy $d > 0$ which we only include for numerical reasons. We do not speculate on the real size of this anisotropy, as there is no experimental information available for it until now. The symbols
(ij) and (ij)' imply summation over nearest-neighbour bonds along and perpendicular to the c-axis.

The starting point of the calculation is the classical Néel state. Perpendicular to the c-direction, the spins form a trigonal lattice structure, subdivided into three interpenetrating sublattices. These sublattices are stacked antiferromagnetically along the c-direction. The ordered system thus contains six sublattices $\mathcal{L}(L, c)$, numbered with $L = 1, 2, 3$ within one plane perpendicular to the c-axis, and with $c = 1, 2$ in the c-direction. In order to describe the Néel state properly, we perform coordinate transformations on each sublattice $\mathcal{L}(L, c)$ such that each $\mathbf{S}_i$ points into the local z-direction. Parametrizing these transformations by polar and azimuthal angles $\phi_{L,c}$ and $\theta_{L,c}$, we apply a Holstein-Primakoff transformation on the spins and retain only the constant and bilinear parts of the Hamiltonian. After Fourier-transforming $H$, we diagonalize it by a Bogoliubov transformation.

The diagonal form of $H$ then reads

$$H = H_{\text{Néel}} + H_0 + 2S \sum_{L,c} \sum_q \omega_{L,c}(q) \left( a_{q,Lc}^\dagger a_{q,Lc} + \frac{1}{2} \right).$$

$H_0 \propto (S, h)$ contains constants arising from a rearrangement of the bilinear terms of $H$, and $a_{q,Lc} (a_{q,Lc}^\dagger)$ is the Fourier transform of the Holstein-Primakoff boson $a_i (a_i^\dagger)$ on the sublattice $\mathcal{L}(L, c)$. $H_{\text{Néel}} \propto (S^2, h \cdot S)$ contains the classical part of $H$, i.e. the exact Hamiltonian for $S \to \infty$. Minimizing it with respect to the angles $\phi_{L,c}$ and $\theta_{L,c}$ yields the ground-state spin configuration of (2) [16], [17]. The problem of quantum corrections to the ground-state energy may be important for some cases [18], [19].

If the applied field $\mathbf{h}$ does not break the rotational symmetry of (2) in the limit $h = 0$, i.e. for $\mathbf{h}$ parallel to the c-axis, the Néel state is made up of two antiferromagnetically stacked triangular lattices. Within these lattices, the spins of the three sublattices lie on the surface of a cone ($|\phi_{L,c} - \phi_{L,c}'| = 2\pi/3, L \neq L'$) with the axis parallel to the field (the c-axis) and an apex angle $\theta_{L,c} = \theta = \arccos \left( \frac{h/(2S)}{2 + d + (3/2)\Delta} \right)$. The spin-wave dispersion is given by

$$\omega_{L,c}^2(q) = \left( 1 + (-1)^c \cos q_z + \frac{3}{2} \Delta (1 - 2\rho_L(q)) \right) \times$$

$$\times \left( 1 - (-1)^c \left( 1 - 2\cos^2 \Theta + d (1 - \cos^2 \Theta) \right) \cos q_z + \frac{3}{2} \Delta \left( 1 + 4 \left( 1 - \frac{3}{2} \cos^2 \Theta \right) \rho_L(q) \right) \right),$$

$$\rho_L(q) = \frac{1}{3} \left( \cos^2 \left( \frac{q_z}{2} - \Phi_L \right) + \cos \left( \frac{q_z}{2} - \Phi_L \right) \cos \left( \frac{\sqrt{3}q_y}{2} \right) - \frac{1}{2} \right),$$

$\Phi_1 = 0$, $\Phi_2 = \frac{2\pi}{3}$, $\Phi_3 = -\frac{2\pi}{3}$.

With a magnetic field perpendicular to the c-axis, one obtains for a small anisotropy $d$ a so-called umbrella-type spin configuration for $h > h_1 \approx 2S\sqrt{d}$. In the umbrella-phase, the spins cant out of the c-plane—they lie on the surface of two cones with the axis parallel to the field direction, but different apex angles. Since in this case a simple closed-form solution for $\omega_{L,c}(q)$ is not achievable, we diagonalized the Hamiltonian (2) numerically.

Figure 1(c) shows a typical dispersion unfolded in the chemical Brillouin zone for an interchain coupling $\Delta = 0.01$, vanishing uniaxial anisotropy $d$, and vanishing magnetic field. In the directions parallel to the c-axis, the scale is set by the intrachain coupling, which fits the
Fig. 1. – Spin-wave dispersion for the trigonal-chain structure in a magnetic field. a) Field applied perpendicular to the $c$-axis, b) field parallel to the $c$-axis, c) without applied field. The ratio $\Delta$ of interchain-to-intrachain coupling is 0.01.

neutron scattering data on Yb$_4$As$_3$ if we set $J \approx 25$ K, rescaling by a factor of $2/\pi$ according to the Bethe-ansatz result. In the directions transverse to the $c$-axis, the scale of the dispersion of the spin-wave modes is given by $\sqrt{\Delta}$. There are three modes becoming soft at the $\Gamma$-point, corresponding to the continuous degeneracy of the ground state with respect to rotations of all spins by the same angle around an arbitrary axis.

Upon applying a magnetic field, this degeneracy is lifted, and the corresponding modes acquire a finite frequency at the $\Gamma$-point. For an arbitrary small but finite anisotropy $d$, we still have one Goldstone mode if the field is applied parallel to the $c$-axis, corresponding to the independence of the ground state with respect to rotations around that axis, see fig. 1 b).

For a field direction perpendicular to the $c$-axis, a gap opens in the entire Brillouin zone. For $\sqrt{\Delta} \ll h \ll h_s = 2 + 9\Delta/2$, the value of the gap is $E_g/J \approx \sqrt{3}\Delta$. In fig. 1 a) and b), we take $h = 0.2$, corresponding to a magnetic field of about 6 T.

The scenario outlined above allows for an at least qualitative understanding of the behaviour
of the specific heat $C_V$ in a magnetic field as follows. For temperatures $k_B T/J \ll \sqrt{\Delta}$, the crystal behaves “three-dimensionally”, i.e. $C_V \propto T^3$. If $k_B T/J > \sqrt{\Delta}$, the $T$-dependence becomes linear, $C_V \approx \gamma T$, because then interchain excitations are thermally populated, and only the quasi-one-dimensional intrachain excitations contribute. In fig. 2 we show the field dependence of the $\gamma$-coefficient at $k_B T/J = 0.02$ (solid lines) and $k_B T/J = 0.2$ (dashed line).

In a magnetic field parallel to the chains, $\gamma$ is reduced by a factor of 2. In this case, there is still the above-mentioned zero-energy mode giving the main contribution to $\gamma$. If the field direction points perpendicular to the chains, $\gamma$ decreases rapidly as a function of $h$ due to the opening of the gap in $\omega_L(q)$. This rapid decrease compares quite well with the experiment —the experimental values are drawn as open circles in the plot [2]. The experiment was done using a multiple-domain crystal, so one would expect the data to fall between the two extremes, $h$ parallel and $h$ perpendicular to the c-axis.

At temperatures $k_B T/J \gg \sqrt{\Delta}$, the impact of $h$ on $\gamma$ is almost completely suppressed, see the dotted line in fig. 2. Compared with the experimental behaviour of $\gamma(T)$ at sufficiently large fields, this provides us with an order of magnitude for the interchain coupling, i.e. we have $\Delta = \mathcal{O}(10^{-4})$ in order to describe the experiment. The strong dependence of the $\gamma$-coefficient on $\Delta$ is shown in fig. 3. $\gamma$ decreases by almost four orders of magnitude upon variation of $\Delta$ from zero to one, i.e. were $\Delta > \mathcal{O}(10^{-2})$, the characteristic heavy-fermion behaviour of Yb$_4$As$_3$ would not be present.

We conclude that the spin-chain model for Yb$_4$As$_3$ proposed in [10] and its extension discussed here are in excellent agreement with the neutron scattering results of Kohgi et al. and the field dependence of the $\gamma$-coefficient found by Helfrich et al. In particular, it explains very well why this field dependence sets in only at low temperatures. This is due to a new energy scale $\sqrt{JJ'} \ll J$ set by the anisotropy gaps in the excitation spectrum which are caused by the interchain coupling. From the behaviour of $\gamma(H)$ one would obtain
$J'/J \approx 10^{-4}$. In this case it would, however, be impossible to directly observe the branches of excitation propagating transversely to the chain direction (fig. 1) by neutron scattering. We therefore suggest that magnetic-resonance methods which could determine the $\Gamma$-point excitation energies would be very helpful in determining $J'$ and especially $d$ more accurately. Although Yb$_4$As$_3$ is semi-metallic this should not be impossible since the residual resistivity (about $1\text{ m}\Omega\text{ cm}$) is quite large in this compound.

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