Theoretical Model for the Semimetal Yb$_4$As$_3$

Peter Fulde, Burkhard Schmidt, and Peter Thalmeier
Max-Planck-Institut für Physik komplexer Systeme, Dresden, Germany
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Abstract

We present a model which can explain semiquantitatively a number of the unusual properties of Yb$_4$As$_3$. The structural phase transition at $T_c \simeq 300$ K is described by a band Jahn-Teller effect of correlated electrons and is interpreted as a charge ordering of the Yb ions. The low carrier concentration in the low-temperature phase follows from the strong electron correlations of the 4f-holes on the Yb sites and can be viewed as self-doping of charge-ordered chains. The observed heavy-fermion behaviour is on a scale of $T^* \simeq 50$ K and is due to spinon-like excitations in the Yb$^{3+}$-chains. The appearance of a second low-energy scale around 0.2 K is due to the Fermi energy of the low-density carriers.
The rare-earth pnictide Yb$_4$As$_3$ is a material with unusual physical properties\cite{1,2}. At $T_c \simeq 300$ K, a structural phase transition has been observed which is accompanied by a charge ordering of the Yb ions and by discontinuities of the resistivity and the Hall coefficient. The high-temperature phase has the anti-Th$_3$P$_4$ structure with space group I$\overline{4}3d$, while the one of the trigonal low-temperature phase is labelled R3c. Mößbauer spectroscopy data on $^{170}$Yb give clear evidence that below 50 K the system contains about 20\% Yb$^{3+}$ ions characterized by a 4f$^{13}$-configuration and a $J = 7/2$ ground-state multiplet. This fraction is close to the expected value of 25\% if perfect charge ordering takes place with the remaining 75\% Yb-ions in a Yb$^{2+}$- or 4f$^{14}$-configuration. No indication of magnetic ordering is found down to 0.045 K\cite{1}. Instead, the material shows typical heavy-fermion behaviour with a linear specific-heat coefficient $\gamma \simeq 200$ mJ/mol K$^2$ and a correspondingly large spin susceptibility $\chi_S$. The Sommerfeld-Wilson ratio is found to be of order unity, clearly indicating Fermi-liquid behaviour. However, below 2 K the susceptibility rises again, pointing to the presence of another low-energy scale\cite{1,4}. In agreement with the Fermi-liquid behaviour the resistivity is found to be of the form $\rho(T) = \rho_0 + AT^2$ at low temperatures with a ratio $A/\gamma^\nu$ ($\nu \simeq 2$) similar to that of other heavy-fermion systems\cite{2}.

An unusual feature of Yb$_4$As$_3$ is that the heavy-fermion properties arise even though the density of charge carriers is extremely low. The low-temperature Hall coefficient $R_H$ is positive, implying hole conduction and has a value of $(ecR_H)^{-1} = 7 \cdot 10^{18}$ cm$^{-3}$. Thus the density of charge carrier is of order 0.001/Yb-atom. Although Yb$_4$As$_3$ is often referred to as a “low-carrier Kondo system”, it is very suggestive from the above that the heavy-fermion like behaviour of the system must be of different origin than in Kondo-lattice systems. (For reviews see, e.g.,\cite{5,8}.) In fact, we are suggesting that it is unrelated to the Kondo effect.

In the following we describe a model which can qualitatively (and semiquantitatively) explain a number of the unusual properties of the material, in particular the low carrier-density. It differs from the one suggested in\cite{2} which is based on a slightly depleted pnictogen band crossing a narrow Yb 4f band of width $\sim 50$ K. (The latter is assumed to have one hole per eight Yb ions.) Our model is based on a band Jahn-Teller effect of correlated electrons (CBJT) and rests on the following basic assumptions:

- The fifty-six Yb 4f-bands have an overall width of $\sim 0.2$ eV which arises from effective f-f hopping via hybridization with pnictide valence states\cite{3}. In Yb$_4$As$_3$ all Yb-atoms are located on four families of chains oriented along the space diagonals of the cubic unit cell\cite{9}. To reduce the complexity of the f-bands we make the assumption that they can be described by four degenerate one-dimensional bands associated with the chains. Such a model is rather similar to the Labbé-Friedel model for 3d states in A$_{15}$ compounds\cite{11} where one has chains parallel to the cubic axes. Although such models may not be literally true due to interchain coupling, they describe the important aspect that a strain coupling to the one-dimensional band states may easily lead to distortions of the cubic structure and simultaneous repopulation among 4f band states of Yb$_4$As$_3$.

- There is a strong deformation potential coupling typical for mixed-valent systems which removes this degeneracy by a trigonal CBJT-distortion. When the Jahn-Teller transition takes place, the crystal shrinks in the (111)-direction, lifting the four-fold degeneracy. The four equivalent chains are subdivided into one along the (111)-direction, for simplicity referred to as short chain, and the three remaining chains referred to as long...
chains. Since the Yb$^{3+}$ ions have a smaller radius than the Yb$^{2+}$ ones, it is natural to think of the CBJT transition being related to the ordering of Yb$^{3+}$ ions along the space diagonal $\langle 111 \rangle$.

We describe the CBJT transition by an effective Hamiltonian of the form

$$H = -t \sum_{\mu=1}^{\mu_t} \sum_{\langle ij \rangle} f_{i\mu\sigma}^\dagger f_{j\mu\sigma} + \epsilon_{\Gamma} \sum_{\mu=1}^{\mu_t} \Delta_{\mu} f_{i\mu\sigma}^\dagger f_{i\mu\sigma} + N_{L} \mu \epsilon_{0} \epsilon_{\Gamma}^{2},$$  \hspace{1cm} (1a)

where $\mu$ labels the summation over the $\mu_t = 4$ different chains, and $\langle ij \rangle$ denotes a summation over nearest-neighbour sites along one chain. The $f_{i\mu\sigma}^\dagger$ create f-holes with spin $\sigma$ at site $i$ of chain $\mu$. We choose a bandwidth $4t = 0.2$ eV as obtained from LDA calculations \[9\] and, for simplicity, an effective spin degeneracy of $2S + 1 = 2$. The second term in (1a) describes the volume-conserving coupling of the trigonal strain $\epsilon_{\Gamma}$ ($\Gamma \equiv \Gamma_5$) to the f-bands characterized by a deformation potential $\Delta_{\mu} = \Delta (\delta_{\mu 1} - (1 - \delta_{\mu 1}) \frac{1}{\mu - 1})$. \hspace{1cm} (1b)

We assume that changes of the bandwidths due to the distortion are small and can be neglected. The third term in (1a) is the elastic energy associated with the distortion. Here $N_{L}$ is the number of sites in a chain and $c_0$ is the background elastic constant for one chain for which we choose $c_0/\Omega = 10^{11}$ erg/cm$^3$, where $\Omega$ is the volume of a unit cell. (The lattice constant is $a = 8.789$ Å.) Note that the bulk elastic constant $c_0^{\Gamma} = 4c_0$. An elastic constant of this size is common for rare-earth systems, but for Yb$_4$As$_3$ it has not yet been measured.

The Hamiltonian (1) does not yet contain the strong Coulomb interactions of holes at an Yb site. Therefore it is reasonable only above $T_c$ where the number of holes per Yb site is $1/4$ and somewhat below $T_c$. At low temperatures the Coulomb interactions and the strong correlations which they imply are crucial (see below). However, for modeling the CBJT phase transition the Hamiltonian (1) is sufficient. The condition for a phase transition to occur is $\Delta^2/(4tc_0) > 3$. We choose $\Delta = 5$ eV, which corresponds to a reasonable Grüneisen parameter $\Omega \equiv \Delta/(4t) = 25$. From this, a transition temperature of $T_c \simeq 250$ K is obtained which is close to the observed $T_{c}^{\exp} \simeq 300$ K.

Below the phase transition, one obtains a strain order parameter $\epsilon_{\Gamma}(T)$ whose temperature variation together with the band occupation $n_{\mu}(T)$ is shown in Fig. [1]. At $T_c$, the four degenerate bands split with an associated shift of holes from the upper threefold degenerate bands into the lower fourth band. The energy difference between the respective band centers is $\frac{4}{3}\epsilon_{\Gamma}\Delta$. The equilibrium strain at low temperature is $\epsilon_{\Gamma} = -\Delta/(8c_0) \simeq -0.02$. The increase in the hole occupation number of the lower band shows a similar behaviour as $|\epsilon_{\Gamma}(T)|$ until at low $T$ the upper bands are empty (of holes) while the lower band is becoming half-filled.

As the lower band is approaching half-filling, the strong on-site f electron correlations become more and more important. Together with the coupling between short and long chains, this has important consequences as we will demonstrate. We incorporate the strong correlations by an on-site Hubbard interaction $U$ which can be eliminated by going over to a t-J Hamiltonian of the form

\[3\]
FIG. 1. Temperature dependence of the strain order parameter $\epsilon_{\Gamma}(T)$. Inset: Occupation numbers $n_\mu(T)$ of the four $f$-bands.

\[
H^{(1)} = -t \sum_{\langle ij \rangle \sigma} \mathcal{P} f_{i1\sigma}^\dagger f_{j1\sigma} \mathcal{P} + J \sum_{\langle ij \rangle} \left( S_i^{(1)} \cdot S_j^{(1)} - \frac{1}{4} n_i^{(1)} n_j^{(1)} \right),
\]

where $J = 4t^2/U$ and $S_i^{(\mu)} = \sum_{\alpha\beta} f_{i\mu\alpha}^{\dagger} \sigma_{\alpha\beta} f_{i\mu\beta}$, $n_i^{(\mu)} = \sum_\sigma n_{i\sigma}^{(\mu)}$. With $U = 10$ eV, we obtain $J \approx 1 \cdot 10^{-3}$ eV. The projector $\mathcal{P}$ serves for the projection onto singly occupied sites. We make use of the so-called slave-boson approximation \cite{2,3}, representing the projector $\mathcal{P}$ by auxiliary bosons $b_j$. The projection back onto the physical states of the now enlarged Hilbert space is done by means of Lagrange multipliers $i\lambda_j$ for each site $j$. We introduce two Hubbard-Stratonovič fields $\chi_{ij} = \langle \sum_\sigma f_{i1\sigma}^{\dagger} f_{j1\sigma} \rangle$ and $r_j = \langle b_j \rangle$ to decouple the Hamiltonian (2), assuming that we work in a range of parameters where we can ignore Cooper pairing by setting $\langle f_{i1\uparrow}^{\dagger} f_{j1\downarrow}^{\dagger} - f_{i1\downarrow}^{\dagger} f_{j1\uparrow}^{\dagger} \rangle = 0$. ($\langle S_i^{(1)} \rangle = 0$ as well.) Performing the uniform-saddle point approximation, $\chi_{ij} = \chi$, $r_j = r$, $i\lambda_j = \lambda$, the Hamiltonian becomes after Fourier transformation

\[
H_{MF}^{(1)} = \sum_{k\sigma} \xi_k f_{k1\sigma}^{\dagger} f_{k1\sigma} + N_L \left( \frac{3}{4} J \chi^2 - \lambda \left( 1 - r^2 \right) - \frac{1}{2} J \left( 1 - r^2 \right)^2 \right),
\]

\[
\xi_k = -2 \left( r^2 t + \frac{3}{4} J \chi \right) \cos k + \lambda + \frac{3}{4} J
\]

The variational equations for the mean-field parameters lead to $r^2 = \delta$ (where $\delta$ is the deviation from half-filling of chain 1), $\lambda = 2t\chi$, and $\chi(T = 0) = \frac{2}{\pi} \sin \left( \frac{\pi}{2} (1 - \delta) \right)$. We observe that for low temperatures, the thermodynamics is essentially governed by a renormalization of the effective mass of the lower band,

\[
\frac{m^*}{m_b} = \frac{t}{\delta t + \frac{3}{4} \chi J} \approx 1.0 \cdot 10^2,
\]

where $m_b$ is the bare band mass. This value for $m^*$ corresponds to a spinon bandwidth of 25 K, which is close to the experimental $T^*$. 

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This brings us to an important point, namely the determination of the quantity $\delta$ in the limit of $T \to 0$. Without interchain coupling, the upper three bands are empty (of holes) in that limit, while the lower band is half-filled. The system should be a Mott-Hubbard insulator in that case. This changes when the interchain coupling is taken into account. In order to appreciate this point we neglect first the correlations. We introduce transversal hopping matrix elements $t'_{\perp} \epsilon_T$ induced by the distortion between the short chain and the other three chains. These are again effective matrix elements, because the Yb-Yb hopping is viewed as taking place via intermediate pnictogen states. We have scaled $t'_{\perp}$ with the strain to be able to restore the cubic symmetry at $T \geq T_c$. Then we have to find new single-particle eigenstates $\phi_{k\lambda \sigma}^\dagger = \sum_\mu e_{\delta \mu}(k) f_{k\mu \sigma}^\dagger$ and the corresponding eigenvalues. The latter result is an additional repulsion of the lower and upper bands by an amount of $9t'^2/(4\Delta)$. The lower band is still half-filled, but when the strong correlations are taken into account, this does no longer imply a Mott-Hubbard insulating behaviour. Instead, the hole count on the short chain is reduced to

$$n_{\mu=1} = \frac{1}{N_L} \sum_{k\sigma} |e_{11}(k)|^2 \langle \phi_{k1\sigma}^\dagger \phi_{k1\sigma} \rangle \simeq 1 - \frac{27}{16} \left( \frac{t'_{\perp}}{\Delta} \right)^2,$$

since the single-particle eigenstates $\phi_{k\lambda \sigma}$ contain contributions $\propto t'_{\perp}/\Delta$ from the long chains. The Hubbard-$U$ has an effect only in the short chains where the hole concentration is nearly 1, but not in the long chains where the hole density is very small. Therefore the system acts like being self-doped with a doping parameter $\delta = \frac{27}{16} \left( \frac{t'_{\perp}}{\Delta} \right)^2$. Taking $\delta \simeq 0.6 \cdot 10^{-3}$ from experiment, we have $t'_{\perp} \simeq 0.1 \text{ eV}$. Note that the self-doping found here differs from the one, e.g., in YBa$_2$Cu$_3$O$_7$ where holes are transferred from the Cu$^{3+}$ ions in the chains to the Cu$^{2+}$ ions in the planes because several bands are crossing the Fermi level.

With the picture outlined above one can understand, at least qualitatively, a number of properties of Yb$_2$As$_3$. The large $\gamma$-coefficient results from the (spinon-like) excitations within the short chains. We obtain it formally from the large mass enhancement (4). The same holds true for the spin susceptibility. At this point it should be noted that our model contains a second temperature scale, which is given by the Fermi energy $\varepsilon_F^b$ of the holes in the long chains. For $\delta \simeq 0.6 \cdot 10^{-3}/\text{Yb-atom}$ we find $\varepsilon_F^b \simeq 0.2 \text{ K}$. This might explain the low-temperature behaviour of $\chi_S(T)$, because the holes in the long chains give rise to a Curie-like susceptibility except at $k_B T \ll \varepsilon_F^b$ when the Fermi gas becomes degenerate.

As far as transport is concerned, we expect that the same heavy quasiparticles responsible for the large $\gamma$-coefficient are also governing the low-$T$ behaviour of the resistivity. The resistivity of the short chains is presumably higher than the one of the holes in the long chains. In a crystal with different domains the one of the short chains will therefore make the largest contribution to the measured resistivity. This might explain why the prefactor $A$ of the $T^2$-term leads to a value for the ratio $A/\gamma^2$ like in other heavy-fermion systems (4). As far as $\rho(T)$ for $T \lesssim T_c$ is concerned, it must increase with decreasing temperature because of the depletion of holes in the upper bands. Thus $\rho(T)$ must have a maximum in order to match on to the $\rho_0 + AT^2$ behaviour at low $T$. Concerning the Hall coefficient, we expect that in the presence of different channels with different conductivities $\sigma_\mu$ the one with the largest $\sigma$ makes the biggest contribution (4). This would imply that the holes in the long chains are most effective here. Since the hole density increases with rising $T$,
the Hall coefficient decreases accordingly. The initial increase for small temperatures is possibly an effect beyond the simple one-band model expression for the Hall coefficient. It is worth noticing that in the high-temperature phase the experimental Hall coefficient is 
\[(ecR_H)^{-1} = 1 \cdot 10^{21} \text{ cm}^{-3}\]. With a volume \(\Omega = 6.8 \cdot 10^{-22} \text{ cm}^3\) per unit cell, this would correspond to 0.25 holes per formula unit Yb\(_4\)As\(_3\) provided we have a one-band system. With four independent bands the application of a generalized theory for the Hall coefficient \([15]\) yields one hole per formula unit, as expected from a chemical approach using valence electron counting.

In conclusion we may state that the model presented here for Yb\(_4\)As\(_3\) explains semiquantitatively the most important experimental findings in a natural way. Among them are the low carrier concentration in the low-temperature phase, the heavy-fermion behaviour with an effective mass ratio \(m^*/m \simeq 100\) as well as the appearance of a second low-energy scale of order 0.2 K.

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