Proceedings of the European Conference Physics of Magnetism, Poznań 2017

Localized f Electron Aspect in Heavy-Fermion Intermetallic $YbRh_2Si_2$

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We point out that there is more and more experiments showing the almost perfect localization of thirteen f-electrons in the canonical heavy-fermion system: $YbRh_2Si_2$. The revealing of the Yb^{3+} crystal-field (CEF) states confirms the Quantum Atomistic Solid State Theory. QUASST was the only theory, which has claimed from 1992 the existence of the discrete CEF electronic structure and the Kramers doublet ground state in heavy-fermion intermetallics. The removal of the on-site Kramers degeneracy via spin-dependent interactions is origin of the large specific heat at low temperatures (a hallmark of the heavy-fermion phenomena) and of low-energy neutral spin-like excitations. The Kondo resonance is related to the slight splitting of the Kramers doublet ground state of the Yb^{3+} ion.

DOI: 10.12693/APhysPolA.133.387

PACS/topics: Heavy fermion, crystal field, Kondo resonance, $YbRh_2Si_2$

1. Introduction

There is more and more experiments showing the almost perfect localization of thirteen f-electrons in the canonical heavy-fermion (h-f) system: $YbRh_2Si_2$. The revealing of the Yb^{3+} crystal-field (CEF) states confirms the quantum atomistic solid state theory (QUASST) worked out by Radwanski *et al.* [1, 2]). QUASST was the only theory, which has claimed already from 1992 the existence of the discrete CEF electronic structure and the Kramers doublet ground state in heavy-fermion (h-f) intermetallics like it is in conventional rare-earth intermetallics, e.g. $ErNi_5$ [3]. In fact, such CEF studies in intermetallics have been started with Prof. J.J.M. Franse in 1985 at the University of Amsterdam, with successfull description of high-field magnetization curves of Ho_2Co_{17} revealing single-ion crystal-field origin of the magnetocrystalline anisotropy [4, 5].

The aim of this paper is to check how well the magnetic and electronic properties of $YbRh_2Si_2$ are understood and described within the Quantum Atomistic Solid-State Theory. Moreover, we would like to remind the Polish contribution to the understanding of the heavy-fermion problem — the more that it turns out to be the correct one.

2. Some experimental facts

$YbRh_2Si_2$ exhibits large low-temperature specific heat with the Sommerfeld coefficient γ_{el} = 500 mJ/K mol at T = 1 K (1990) and 1000 mJ/Kmol at T = 0.1 K (2002) [6, 7]. Low-temperature specific-heat measurements yields Kondo temperature as 25–30 K [8]. Sichelschmidt *et al.* [9] in 2003 has observed the electron spin resonance (ESR) at 1.5 K with very anisotropic g factor: ($g_\perp = 3.56$ (B_{res} = 0.188 T) and $g_\parallel = 0.17 \pm 0.07$ at 5 K). Stokert *et al.* [10] in 2006 have observed by inelastic neutron scattering localized CEF excitations of 17, 25 and 43 meV. $YbRh_2Si_2$ orders antiferromagnetically at ultra-low temperature 70 mK [8] and exhibits the nuclear magnetic ordering at 2 mK coexisting with a superconducting state below 10 mK [11].

Observation in the Steglich group of the first successful electron spin resonance (ESR) on single crystalline was very suprising as it provided a strong indication for the localized f states in this profound heavy-fermion metallic compound. The importance of this result has relied in the fact, that practically all theories devoted to heavy-fermion phenomena were taking in Kondo and heavy-fermion intermetallics the itinerant or band behavior of f electrons as the starting point. Theoretical approaches to heavy-fermion phenomena with localized f states and the Kramers doublet ground state were not in fashion [12].

3. Some historical facts

In the abstract of the rejected paper O3 in PM-1993 [12] one can read: "It will be proposed to discuss the h-f compounds in terms of physical concepts worked out for rare-earth intermetallics [3]. To remind, the magnetic and electronic properties of rare-earth intermetallics are understood by considering a few, two in the simplest but quite adequate approach, electronic subsystems i.e. the f electronic subsystem and conduction-electron subsystem (the individualized-electron model). These two subsystems are described by essentially different theoretical approaches referring to the localized and band magnetism. In view of the individualized-electron model the large specific heat originates from low-energy excitations between doublet levels of the Kramers state of the f^n electronic subsystems that are slightly split due to exchange interactions. These excitations are many-electron excitations in contrary to single-electron excita-

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tions in the conduction-electron subsystem. One can say that the h-f compounds are compounds with Kramers f ions that have difficulties, due to exotic ground state and weakness of exchange interactions, to form the well-established magnetic order. However, the system has to release the Kramers entropy before reaching zero temperature as is experimentally observed by the entropy value of $R \ln 2$."

Such the Kramers doublet ground state of the f^{13} electronic system (Yb^{3+} ion) has been just revealed by ESR in $YbRh_2Si_2$.

In, say, a year of 1993 it was believed that crystal-field states, if at all exist in intermetallics, will be somehow washed out below the Kondo temperature by the hybrydization with conduction electrons. As was written by Si *et al.* [13], the famous American theoretician, "The microscopic model we consider is the Kondo lattice model. At each lattice site, a local moment interacts via an exchange coupling J_K with the spin of any conduction electron sitting at the site. There are two important energy scales in the problem: The Kondo temperature T_K sets the scale below which an isolated local moment would be screened by the spins of the conduction electrons, while the RKKY interaction characterizes the induced coupling between two local moments." In the Kondo lattice model the large specific heat has been explained as related with the formation of the Kondo resonace at the Fermi level by the hybridization of f electrons with conduction electrons. By the hybridization f electrons become itinerant because the occupation of f states is not any longer integer, i. e. the internal ionic integrity is broken.

Thus one of us (RJR) admits that indeed he by all his scientific research was searching for the crystal field everywhere [14–16]. He has pointed out the substantial physical adequacy of the atomic-like localized crystal-field states, the detailed local symmetry, importance of the intra-atomic spin-orbit coupling and the orbital magnetism both for $4f/5f$ intermetallics and $3d$-ion compounds. After 30 years he says that according to him the existence of the crystal-field states in $3d/4f/5f/4d/5d$ is in the 2017 year quite generally established within solid-state experimentalists and he strongly recommends young physicists, both experimentalists and theoreticians, to learn much of the crystal field, inspect the local symmetry and the group theory.

The discovery by the Prof. F. Steglich group of ESR in $YbRh_2Si_2$ at temperatures more than 15 times lower than T_K was really of the great importance for the theoretical understanding of heavy-fermion phenomena. Immediately after the publication (6 October 2003) of the ESR result one of us (RJR, noting it 26 December) has derived the relevant CEF parameters (31 December 2003) and the Kramers-doublet ground-state eigenfunctionin a form [17]:

$$\Gamma_7^1 = 0.803|\pm 3/2\rangle + 0.595|\mp 5/2\rangle$$
$$-0.027|\mp 1/2\rangle - 0.009|\pm 7/2\rangle. \quad (1)$$

This ground-state Kramers doublet reproduced perfectly the experimental g factors within the crystal-field interactions for the Yb^{3+} ion. Inspecting at present the literature it seems that these submissions were the first detailed explanation of the ESR result in $YbRh_2Si_2$. The shown ground state of the Yb^{3+} ion in $YbRh_2Si_2$ is at present generally accepted [18, 19].

4. Theoretical outline

We point out at the start that transition-metal atoms with incomplete $3d/4f/5f/4d/5d$ shell preserve their atomic-like integrity also in a solid — thus we have named our approach as the QUASST [1, 2]. It has much in common with the crystal-field theory, being however extension in order to account for the formation of the magnetic state. It has been formulated in times when the crystal field was not in-fashion within the Magnetic and Kondo/heavy-fermion community. Pointing out the importance of the crystal field we underline that a theoretical description of exotic intermetallics with fictitious (isotropic) spins $s = 1/2$ in, for instance, Fermi-liquid theories is an oversimplificied approach.

The Yb^{3+} has 13 f electrons in the incomplete f shell forming according to us the strongly-correlated atomic-like $4f^{13}$ configuration. The Hund rule ground multiplet of the Yb^{3+} ion is $^2F_{7/2}$ being described by $J = 7/2$ (the higher multiplet $^2F_{5/2}$ lies, due to strong spin-orbit interactions, 1.3 eV (15 000 K) above and does not affect low- and ambient-temperature properties). The crystal field of the tetragonal symmetry contains 5 parameters and splits the 8-fold degenerated multiplet $^2F_{7/2}$ into 4 Kramers doublets, two Γ_6 and two Γ_7 [17, 18]:

$$\Gamma_7^1 = \sin\beta|\pm 3/2\rangle + \cos\beta|\mp 5/2\rangle. \quad (2)$$

For the eigenfunction of Eq. 2

$$g_\perp = 2g_J\sqrt{3}\sin(2\beta); \quad g_\parallel = g_J(4\sin^2\beta - 2.5), \quad (3)$$

where $g_J = 8/7$. β of 54.5° yields $g_\parallel = 0.17$ and $g_\perp = 3.74$ close to experimental results confirming the single-ion origin of the ESR signal. It is unbelieved that so simple considerations predict so consistently the eigenfunction of the ground state. Thus the problem is to find such set of CEF parameters which puts the state Eq. 3 the lowest and simultaneously reproduces the g tensor and INS excitations 17, 25 and 43 meV [10] and 17.9, 25.2 and 40.8 meV reported by Stock *et al.* [19].

5. Results and discussion

We have obtained a set of CEF parameters: $B_2^0 = 6.0$ K, $B_4^0 = +138$ mK, $B_6^0 = -5.5$ mK, $B_4^4 = -417$ mK and $B_6^4 = 140$ mK [19]. This set yields energy levels at 204 K (17.6 meV, Γ_6^1), 303 K (=26.1 meV, Γ_7^2) and 491 K (42.3 meV, Γ_6^2) as well as $g_\perp = \pm 3.80$, $g_\parallel = \pm 0.160$ for the Kramer doublet ground state Γ_7^1.

Introduction of a small local orthorhombic distortion $B_2^2 = 0.7$ K makes an improvement of the g tensor to $g_\perp = \pm 3.61$, $g_\parallel = \pm 0.157$. A larger plane distortion $B_2^2 = 1.1$ K yields $g_\perp = \pm 3.50$, $g_\parallel = \pm 0.155$ leaving the energy states unchanged, i.e. 205, 303 and 491.5 K.

Thus the set of CEF parameters nicely resembles the experimental findings. A smaller value of $g_\parallel$ than 0.17 is accepted noting that this value is charged with a large experimental error ± 0.07 [9]. The appearrance of a in-plane anisotropy is quite acceptable, the more that it is very small. We think that this orthorhombic distortion is a reason for the observed reduction of $g_\perp$ from 3.60 at 20 K to 3.50 at 2 K [9, 20]. This distortion in our calculations grows with the lowering temperature what is consistent with a general rule.

We turn to the problem of low-energy excitations which are origin of large specific heat below the Kondo temperature. We agree with authors of Ref. [14] that "the most fundamental question regarding any condensed matter system concerns the nature of their low-energy excitations." Indeed, it is the main problem of heavy-fermion phenomena exhibiting large Sommerfeld coefficient in the low-temperature specific heat. This problem is strongly related to the Kondo resonance which appears in the Kondo-lattice model [14, 21] at the Fermi level. According to that, the Kondo resonance is related to the slight splitting of the on-site Kramers doublet - the splitting is undoubtedly due to the spin-dependent interactions. In the specific-heat experiment the lowest Kramers-doublet state looks like to lie at the Fermi level. The removal of the Kramers degeneracy is a source of low-energy, below 0.2 meV, excitations - one can call it as quasiparticles. The Kondo resonance in Ref. [20] is extremely and artificially narrow - according to that it is the splitting of the Kramers doublet. In our QUASST model these low-energy excitations are neutral, spin-like excitations to the slightly split Kramers-doublet conjugate state. These excitations manifest by large low-temperature specific heat, a hallmark of heavy-fermion physics.

The local moment associated with two Kramers conjugate states have the opposite directions. The local moment causes the spin-polarization of conduction electrons whereas the Kondo-type interactions bind this spin polarization antiparallelly to the local moment. A thermal excitation to the Kramers conjugate-state is associated with the full reversal of the local moment engaging also the reversal of the spin-polarization of conduction electrons making these excitations "heavy". Such thermally-induced quasiparticles can propagate through the lattice though f electrons stay localized. At any temperature and at given site only one state of the Kramers doublet is occupied. The realized CEF states are many-electron states (of all 13 f electrons in the ion) in contrary to single-electron states usually considered in first-principles calculations.

6. Conclusions

We have derived CEF parameters of the tetragonal symmetry with a small orthorhombic distortion that perfectly reproduce the ESR values ($g_\perp = 3.56$ and $g_\parallel = 0.17$) as well as excitations observed in inelastic-neutron-scattering experiments with the Γ_7^1 Kramers-doublet ground state of the Yb^{3+} ion in $YbRh_2Si_2$. According to us, the Kondo resonance is related to the slight splitting of the on-site Kramers doublet ground state. In the specific-heat experiment the lowest Kramers-doublet state looks like to lie at the Fermi level. The removal of the Kramers degeneracy is a source of low-energy, below 0.2 meV, excitations. In our QUASST model these low-energy excitations are neutral, spin-like excitations to the slightly split Kramers-doublet conjugate state. These excitations are observable as large low-temperature specific heat, a hallmark of heavy-fermion physics. Moreover, according to us the whole present progress in the theory of the solid-state physics proceeds in the evaluation of the crystal-field states in $3d/4f/5f$ ionic and metallic compounds and in an implementation of the many-electron crystal field to so-called *ab-initio*/first-principles computer programma. The QUASST and first-principles calculations will meet in the detailed description of the charge distribution in the given compound and of real discrete energy states, in the meV-energy scale, realized in this compound.

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