Spin-glass transition as the cause of a false heavy-fermion behavior of the YbH$_x$ system

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(Submitted 8 July 1993)
Pis'ma Zh. Eksp. Teor. Fiz. **58**, No. 4, 276–279 (25 August 1993)

Ytterbium ions in the cubic phase of YbH$_x$ have a well-defined magnetic moment according to ESR measurements. A transition to a spin-glass state has been observed at $T \sim 8$ K. The low-temperature anomalies which have been seen previously in the specific heat and magnetic susceptibility, and which suggested that this is a heavy-fermion system, are very probably due to a magnetic transition.

1. The gradual transition of the magnetic susceptibility from a Curie–Weiss behavior to a Pauli behavior as the temperature is lowered, the peak in the specific heat, and the linear behavior of the specific heat at low temperatures are characteristic of Kondo fluctuations in compounds of the rare-earth elements Ce and Yb, in which the 4*f* level is fairly close to the Fermi level. On the other hand, these anomalies in the behavior of integrated characteristics are far from sufficient evidence for drawing the conclusion that a specific substance is of a heavy-fermion nature. A similar behavior of the specific heat and the static susceptibility can be observed in systems with stable local moments near a spin-glass magnetic transition. Gschneider *et al.*[1] have pointed out some possible examples of systems in which a spin-glass magnetic transition can simulate a heavy-fermion behavior in this sense.

The similarities in the behavior of thermodynamic properties of Kondo systems and of spin glasses (and also in RVB spin systems with a short-range order[2]) is not surprising. It is becoming clear [(Ref. 3) for example] that the entropy of a Kondo system approaches a purely spin nature below Kondo temperature T_C. The linear specific heat can be found by describing the spin subsystem as a set of two-level systems in which the distance between the energy levels is distributed over a scale $\Delta E \leqslant k_B T_C$.[4] This situation is highly reminiscent of that in spin glasses, in which the low-temperature specific heat (below the freezing temperature T_f) is determined by frustrated spins in random fields which are distributed over the interval $\omega < k_B T_f$, where k_B is the Boltzmann constant. A reliable identification of a particular system is possible only if the dynamic characteristics of the local moment are known. The ESR method is effective in this sense. For example, if an ESR signal from 4f electrons is observed, one can definitely rule out a heavy-fermion behavior, since in a system with quantum Kondo fluctuations with a frequency $\omega \sim k_B T_f$ it would be impossible to observe an ESR because of a broadening of the resonance line.

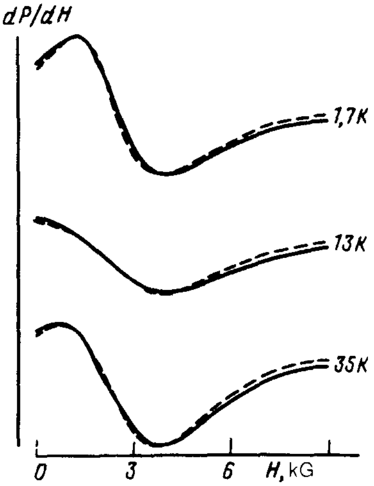

FIG. 1. ESR spectra of a $YbH_{2.37}$ sample at various temperatures. The dashed lines are lineshapes calculated in accordance with Eq. (1).

In this letter we report the observation of an ESR signal of ytterbium ions in the cubic phase of ytterbium hydride, $YbH_x(2.25<x<2.6)$, which has previously been assumed to be a nonmagnetic heavy-fermion system on the basis of data on the specific heat and the magnetic susceptibility.[5] The ESR data also indicate a magnetic transition at ~8 K.

2. The dihydride YbH_2 has an orthorhombic structure, in which the ground state of ytterbium is a bivalent nonmagnetic state.[6] The addition of hydrogen puts the system in a cubic phase at $x>2.25$, in which one observes a Curie–Weiss behavior at high temperatures, a saturation of the susceptibility, and a rounded maximum in the specific heat[5] at ~4 K. These effects of hydrogen doping are explained on the basis that the structural transition is accompanied by a sharp change in the position of the $4f$ level with respect to the Fermi level; a magnetic moment arises as a result.

3. Samples of $YbH_{2.37}$, $YbH_{2.41}$, $YbH_{2.55}$, and $YbH_{2.57}$ were synthesized by a direct interaction of gaseous hydrogen with the metal (the Yb purity was ~99.9%). These samples were powders in sealed-off thin-walled quartz cells. Examination by x-ray diffraction revealed that all samples consisted of a single phase and had an fcc lattice. The ESR measurements were carried out in the 3-cm wavelength range on a Bruker BER-418^{s} spectrometer in the temperature range 1.6–300 K.

A broad and intense absorption line was found in the ESR spectra of all the samples studied. Figure 1 shows several typical lines. The observed signals can be described by a Lorentzian lineshape in accordance with expressions written for the case $\Delta H \geqslant H_0$, where ΔH is the linewidth, and H_0 the resonant field:[7]

$$dP/dH \sim d(\chi'' + \alpha\chi')/dH,$$

$$\chi' = (\chi_0/2[A^+ + A^- + H(a^-A^- - a^+A^+)/\Delta H],$$

$$\chi'' = (\chi_0 H_0/2\Delta H)(A^- + A^+),$$

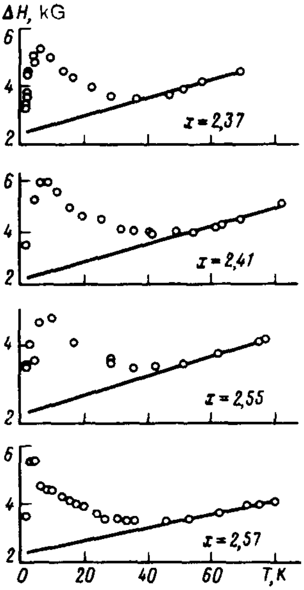

FIG. 2. Temperature dependence of the width of the ESR line of hydrides YbH_x at various hydrogen contents.

$$A^{\pm}=[1+(a^{\pm}/\Delta H)^2]^{-1}, \quad a^{\pm}=(H_0\pm H)/\Delta H. \tag{1}$$

Here H is the external magnetic field, and χ_0 the static magnetic susceptibility. The presence of a dispersion admixture χ' in (1) is characteristic of conducting systems.[8] The coefficient α is determined by the particular distribution of the microwave field; it turned out to be ~ 0.2 in the test samples.

Figure 2 shows curves of the temperature dependence of the linewidth ΔH found through a simulation of the spectra on the basis of expression (1). The line broadens greatly at temperatures above 90 K and cannot be analyzed there. The resonant field turned out to be 2.0 ± 0.1 kG, and essentially independent of the temperature, for all samples. This value corresponds to a g-factor of 3.4, which is close to the g-factor of the Yb^{3+} ion in a cubic crystal field, 3.428. The behavior of the linewidth at temperatures $T>40$ K is described by the linear expression $\Delta H=\Delta H_{\rm res}+bT$ (the straight lines in Fig. 2), indicating a Korringa relaxation mechanism, as is characteristic of localized magnetic moments in metals. Here $\Delta H_{\rm res}$ is the residual linewidth due to dipole interactions and the scattering in g-factors. The temperature dependence of the integrated intensity, which is determined by the magnetic susceptibility, has a Curie-Weiss behavior at $T>15$ K with a negative Curie temperature. The latter lies in the interval $10\ {\rm K}\leqslant|\theta|\leqslant 20$ K, depending on the hydrogen content. At temperatures $T\leqslant 10$ K the intensity of the ESR line is only a weak function of the temperature. It obviously follows from these results that the ytterbium ions in these samples have a well-defined local magnetic moment and that the anomalies seen previously[5] in the specific heat in cubic YbH_x compounds at temperatures ~ 4 K are not due to Kondo fluctuations. An upper limit on the effective temperature of the spin fluctuations can be estimated from the ESR linewidth: $T_{\rm C}<g\beta\Delta H/k_{\rm B}\sim 1$ K (β is the Bohr magneton).

4. It can be seen from Fig. 2 that at $T < 40$ K the temperature dependence of the ESR linewidth deviates from a linear law, and the line begins to broaden. This behavior is characteristic of the onset of a short-range spin order in the system. As the temperature is lowered further, the linewidth reaches a maximum at $T = T_f$ and then decreases sharply. At temperatures $T_f < T < 30$ K the increase in the linewidth obeys a power law, $\Delta H(T) - \Delta H_{\text{res}} - bT \sim \{(T - T_f)/T_f\}^{-P}$, with a critical value $P \simeq 0.4$. These facts, along with the gradual onset of a plateau on the integrated intensity of the ESR signal at $T \sim 10$ K, indicate a transition to a magnetically ordered phase of an antiferromagnetic nature. The resonant behavior in the ordered phase is observed at approximately the same frequency as the ESR signal in the paramagnetic region. This agreement is evidence that the anisotropy fields are weak. Although these results are not sufficient for drawing a definite conclusion about the nature of the magnetic order, the monotonic behavior of the intensity and of the characteristics of the ESR line seem to indicate a "soft" freezing of the spin system into a glassy state at $T \leqslant T_f$. Although ytterbium ions formally occupy a regular cubic lattice, there is a pronounced disorder in this system because of the random distribution of hydrogen among tetrahedral and octahedral interstitial positions in nonstoichiometric YbH_x. The defective nature of the local hydrogen surroundings of the ytterbium ion might lead to a random scatter in the exchange interaction between the latter in terms of magnitude and sign and also to a randomization of the easy-magnetization direction. These circumstances would promote the formation of a spin glass.

5. In summary, the ESR results reveal that the ytterbium ions in the cubic phase of YbH_x have stable magnetic moments, and they lead to the conclusion that the "heavy-fermion" behavior in the specific heat of this system[5] is apparently actually due to a spin-glass transition. We should point out that these statements are not intended to rule out the possibility that some fraction of the ytterbium ions are in either a bivalent or mixed-valence state because of differences in the local hydrogen surroundings, since the absolute value of the integrated intensity of the ESR signal cannot be determined well because of uncertainty in the size of the skin thickness. In addition, the method of a shift of x-ray lines leads to an ytterbium valence of 2.66 on the average over the sample.[9] Smirnov *et al.*[9] suggest that there is an inhomogeneous mixture of Yb^{2+} and Yb^{3+} ions in the cubic phase of YbH_x. Our ESR data do not contradict that suggestion, but the magnetic order of the Yb^{3+} ions which has been observed is definite evidence that we are actually dealing with a purely static mixture: If there were significant (with a rate $\geqslant k_B T_f$) quantum or activation processes for a migration of the valence state through the lattice, we would expect an RVB spin-liquid ground state, rather than a magnetic one.

This study was supported financially by the Russian Basic Research Foundation (Project 93-02-2578).

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Translated by D. Parsons