Quasiquartet CEF ground state with possible quadrupolar ordering in the tetragonal compound YbRu$_2$Ge$_2$

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Abstract

We have investigated the magnetic properties of YbRu$_2$Ge$_2$ by means of magnetic susceptibility $\chi(T)$, specific heat $C(T)$ and electrical resistivity $\rho(T)$ measurements performed on flux grown single crystals. The Curie-Weiss behavior of $\chi(T)$ along the easy plane, the large magnetic entropy at low temperatures and the weak Kondo like increase in $\rho(T)$ proves a stable trivalent Yb state. Anomalies in $C(T)$, $\rho(T)$ and $\chi(T)$ at $T_0 = 10.2$ K, $T_1 = 6.5$ K and $T_2 = 5.7$ K evidence complex ordering phenomena, $T_0$ being larger than the highest Yb magnetic ordering temperature found up to now. The magnetic entropy just above $T_0$ amounts to almost $R\ln 4$, indicating that the crystal electric field (CEF) ground state is a quasiquartet instead of the expected doublet. The behavior at $T_0$ is rather unusual and suggest that this transition is related to quadrupolar ordering, being a consequence of the CEF quasiquartet ground state. The combination of a quasiquartet CEF ground state, a high ordering temperature, and the relevance of quadrupolar interactions makes YbRu$_2$Ge$_2$ a rather unique system among Yb based compounds.

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In intermetallic compounds based on Ce or Yb, the instability of the $f$-shell of these elements allows them to be tuned from a magnetic to a non-magnetic state by changing the chemical composition or by applying pressure. At the crossover from the non-magnetic to the magnetic state, one observes unusual properties like the formation of heavy fermions, the onset of unconventional superconductivity or strong deviation from the Fermi-Liquid behavior usually expected in a metal. A large part of the research in this field was performed on CeT$_2$X$_2$ compounds (T = transition metals, X = Si and Ge) crystallizing in the ThCr$_2$Si$_2$ or a related structure type, because some of these compounds are very close to this crossover. Two prominent examples are CeRu$_2$Si$_2$ [1, 2] and CeRh$_2$Si$_2$ [3], the former is just on the non-magnetic side and shows an unconventional metamagnetic transition from a delocalized to a localized $f$-state, while the later one, although being just on the magnetic side of the crossover, has the highest antiferromagnetic ordering temperature among all Ce-compounds. While all the CeT$_2$X$_2$ compounds have now been thoroughly investigated, much less studies were performed on the Yb-based homologues. For the Yb-compounds with T = Ru, Os, Rh, Ir, only little or nothing is know about their physical properties. YbRh$_2$Si$_2$ [4, 5] was investigated only quite recently, and was found to be located extremely close to the quantum critical point connected with the onset of magnetic ordered state, which leads to very interesting properties and makes this compound one of the most interesting ones in the field of quantum phase transitions. The first investigation of YbIr$_2$Si$_2$ [6] has just been published, it is a heavy fermion system just on the non-magnetic side of the critical point. In search for further interesting Yb-based compounds we synthesized YbRu$_2$Ge$_2$ and investigated its physical properties. To the best of our knowledge only structural data have been reported up to now [7]. Our results revealed a stable trivalent Yb state, rather complex ordering phenomena with 3 successive transitions at $T_0 = 10.2$ K, $T_1 = 6.5$ K and $T_2 = 5.7$ K, and, to our surprise, a quasiquartet crystal field ground state which is a unique situation among YbT$_2$X$_2$ compound. The behavior observed at $T_0$ suggest this transition to be a quadrupolar one, being a consequence of the quasiquartet CEF ground state. The combination of a quasiquartet CEF ground state, a high Yb ordering temperature and the likely relevance of quadrupolar interactions makes YbRu$_2$Ge$_2$ a unique system among Yb-based compounds.

Polycrystalline samples were prepared by a sintering method, while single crystals were grown from a Sn or In flux [8]. XR-powder diffraction pattern of the polycrystals confirmed
FIG. 1: Temperature dependence of magnetic susceptibility of YbRu$_2$Ge$_2$ for magnetic fields $B=1$T, 2T and 5T applied along basal plane. Inset: $T$-dependence of $1/\chi_{ab}$ for $B=2$T.

the ThCr$_2$Si$_2$ (I4/mmm) structure type, a few weak peaks could not be indexed indicating foreign phases with an amount $< 5\%$. Electron probe microanalysis of the single crystals and X-ray powder diffraction pattern taken from crushed single crystals showed that some of the single crystals were single phase YbRu$_2$Ge$_2$, while others had little impurity phase $< 5\%$ at the surfaces. The lattice parameters of our single crystals, $a = 4.2116 (10)$Å and $c = 9.7545(20)$Å were slightly different from those obtained in our polycrystals, $a = 4.2105 (10)$Å and $c = 9.7567 (20)$Å, and differed significantly from those reported in the literature, $a = 4.203 (4)$Å and $c = 9.763 (9)$Å. This suggests the existence either of a significant homogeneity range (likely along the Ge-Ru line) or of Ge-Ru disorder, changes in composition or ordering leading to a decrease of the lattice parameter $a$ and a much weaker increase of $c$.

The magnetic susceptibility in the temperature range 2K-300K and in an applied field from 1T to 5T was measured in a commercial Quantum Design SQUID magnetometer (MPMS). The specific-heat and the resistivity were determined in a commercial PPMS (Quantum Design) equipment using the relaxation method and a four probe ac-technique, respectively. All physical properties reported here were measured on the best single crystals which had no impurities as revealed by optical microscope and electron probe microanalysis as well as a high residual resistivity ratio. The polycrystalline samples showed similar physical properties, but with broader transitions.

The magnetic susceptibility gives a first evidence for a trivalent Yb state. $\chi(T)$ is strongly
FIG. 2: Temperature dependence of magnetic susceptibility of YbRu$_2$Ge$_2$ for magnetic fields B= 1T and 3T applied along c axis. Inset T-dependence of $1/\chi_c$ for B= 1T.

anisotropic, being much larger for field along the basal plane (Fig.1) than field along the c axis (Fig .2). For field along the basal plane, $\chi_{ab}$ follows rather nicely a Curie-Weiss law from 20 K up to room temperature. The slight curvature in the $1/\chi_{ab}(T)$ versus T plot (inset of Fig.1) at low and high temperatures can be attributed to crystal field effects and a very small T independent diamagnetic contribution, respectively. The value of the effective moment between 20 and 300 K, 4.5 $\mu_B$, is very close to the value expected for a trivalent Yb state, 4.54 $\mu_B$. A pronounced drop of $\chi_{ab}(T)$ below $T_1 = 6.5$ K evidence a transition to a magnetically ordered state, while no anomaly is visible around 10 K, the temperature of a pronounced anomaly in C(T) (see below). The susceptibility for field along the c axis, $\chi_c$, is one order of magnitude lower than for field along the basal plane (Fig. 2). The $1/\chi_c(T)$ versus T curve shows a pronounced negative curvature. As a result the slope at 300 K is still slightly smaller ( 20%) than that expected for a free Yb$^{3+}$ state. Such a pronounced curvature in $1/\chi(T)$ for field along the hard axis can be attributed to a rather large overall crystal field splitting. In the related compounds YbIr$_2$Si$_2$ [9] and YbRh$_2$Si$_2$ [10], the highest excited CEF level is indeed above 400 K. At low temperatures, $\chi_c(T)$ shows a significant change of slope at $T_0 = 10.2$ K, followed by a very pronounced decrease below $T_1$.

The results of the specific heat measurements (Fig.3) confirm the trivalent Yb state and the presence of several phase transitions at low temperatures. The plot C/T versus T (Fig.3) evidences three distinct transitions: a large mean field like anomaly at $T_0 = 10.2$ K and two
well resolved and sharp $\lambda$ type anomalies at $T_1 = 6.5$ K and $T_2 = 5.7$ K. All these three transitions were well reproduced in different single crystals, showing that they are intrinsic. The large size of the anomalies confirms a trivalent Yb state with a localized 4$f$ hole which undergoes ordering at low temperatures. Below $T_2$, the decreases of $C/T$ is proportional to $T^2$, as expected for an antiferromagnet, but below 2 K the temperature dependence evolves towards a larger exponent, indicating an exponential suppression of the magnetic excitations related to the presence of an anisotropy gap. Finally, below 1 K, $C/T$ merges into a constant Sommerfeld coefficient $\gamma \approx 100$ mJ/K$^2$mol. The slight upturn below 0.8 K can be attributed to a nuclear Schottky contribution.

The temperature dependence of the normalized resistivity is shown in Fig.4. The resistivity was measured for current in the basal plane. The resistivity ratio $\rho(300K)/\rho(2K) = 22$ is an indicator for the good quality of the sample. The resistivity linearly decreases with temperature from room temperature down to 70 K, shows a minimum around 50 K below which the resistivity increases with decreasing temperature. This increase was sample dependent, in contrast to all other features in $\rho(T)$ which were very reproducible. We tentatively attribute this increase to some weak Kondo type interaction. At 10.2 K $\rho(T)$ exhibits a sharp break in the slope, from a negative one at $T > T_0$ to a positive one at $T < T_0$. The slope in $\rho(T)$ increase further very strongly at $T_1 = 6.5$ K and only slightly more at $T_2 = 5.7$ K.
FIG. 4: Temperature dependence of the resistivity normalized to its value at 300 K. The inset shows $\rho(T)$ from 2 - 15 K. Kinks marked by arrows correspond to transitions at $T_0$, $T_1$ and $T_2$. Thus all the three transitions are also visible in the resistivity. Interestingly, it turns out that there is a quite good correspondence between $C(T)$, $d\rho(T)/dT$ and $d\chi_c(T)/dT$ in the temperature range of the transitions, between 12 K and 2 K. The decrease in $\rho(T)$ below the transition, especially below $T_1$, can be attributed to the freezing out of spin disorder scattering.

The effects of a magnetic field strongly depend on its direction. A field along the hard direction has only little influence: The size and the shape of the anomalies in the specific heat (Fig.3), in the susceptibility (Fig.2) and in the resistivity (not shown) remains unaffected, the only change being the merging of $T_1$ and $T_2$ for field larger than 10 T. All the transition temperatures decreases only slightly with increasing field, by just 20% in 13 T, the shifts being roughly proportional to $B^2$. The effect of a field along the easy plane is much stronger and differs strongly for $T_0$ and $T_1$. $T_1$ is shifted to lower temperature with increasing field (inset of Fig.1), down to 4 K at $B = 5$ T and to below 2 K at 7T (Fig.5), the shift being also roughly proportional to $B^2$. Further on, the decrease observed in $\chi_{ab}(T)$ below $T_1$ is strongly suppressed in field larger than 1 T. A magnetization curve (Inset of Fig.5) reveals that this change in $\chi(T)$ is connected with a small metamagnetic transition, visible as a jump $\Delta M$ of only 0.5$\mu_B$/Yb in the $M$ versus $B$ plot for $T < T_1$. In contrast $M(B)$ display only a very weak curvature for $T_1 < T < T_0$ and is linear for $T > T_0$. This suggests a spin flop like transition to occur at $B = 1.8$ T for $T < T_1$. In contrast, the upper transition $T_0$
FIG. 5: This figure shows the strong dependence of the specific heat on field applied along the Basal plane in a plot C/T versus T for B= 0T, 4T, 7T. Inset shows the metamagnetic transition (arrow) at B=1.8T observed in a magnetization M versus B plot at T= 2K for field along the basal plane.

shifts to higher temperatures with increasing field, up to 12 K at B = 4 T, and broadens (Fig.5). At B = 7 T the specific heat reveal only a broad, Schottky like anomaly, no clear transition. The origin of this unusual behavior will be discussed below.

Up to now, except for the unusual behavior at T₀, YbRu₂Ge₂ seems to present the classical behavior of a trivalent Yb-compound. The surprise came when we looked at the magnetic entropy S(T), which we calculated by integrating the measured C(T)/T (inset of Fig.3). Because LuRu₂Ge₂ does not form, it was not possible to determine and subtract the phonon contribution to the C(T). However, for the calculation of S(T) in the temperature range considered here (T < 12 K), the phonon contribution can be safely neglected because its contribution is negligible. As an example, the total entropy of the non-magnetic compound LuRh₂Si₂ at 12 K amounts to 0.17 J/molK, less than 2% of the total entropy we determined for YbRu₂Ge₂ at the same temperature. In a tetragonal environment, the crystal field splits the J = 7/2 state of Yb³⁺ into four Kramer doublets, with an energy spacing usually larger than 50 K. Thus only the lowest doublet is relevant for the magnetic properties at low temperatures and one expects S(T) close to Rln2 slightly above T_N. Our surprising result is that the magnetic entropy of YbRu₂Ge₂ just above the highest transition T₀ is much larger, it almost reaches Rln4. This result, which was reproduced with different
samples, proves that in YbRu$_2$Ge$_2$, by accident, the first excited crystal field doublet is almost degenerated with the ground state doublet, the excitation energy being less than 10 K. After our observation we looked in the literature, and found that for the homologue and isoelectronic compound YbRu$_2$Si$_2$, a CEF calculation based on an extrapolation of the CEF scheme of other RRu$_2$Si$_2$ compounds (R = Rare earth) postulated a small excitation energy (25 K) for the first excited CEF level. However, there is up to now no experimental confirmation of such a low level splitting in YbRu$_2$Si$_2$. Thus our investigation reveals a very unusual quasiquartet CEF ground state in YbRu$_2$Ge$_2$, which is unique among YbT$_2$X$_2$ compounds.

With the presence of a quasiquartet CEF ground state, quadrupolar ordering became relevant and has to be considered. For the transition $T_1$, the situation is rather obvious: the strong decrease of $\chi_{ab}(T)$ and $\chi_{c}(T)$ below $T_1$ indicate that this transition corresponds to antiferromagnetic ordering. As a consequence, the transition at $T_2$ is likely related to a change of the magnetic structure. In contrast, for $T_0$ the situation is much less clear. At first we note that $T_0$ is larger than the highest magnetic ordering temperature reported up to now in intermetallic Yb compounds, $T_N = 7.5$ K in Yb$_3$Cu$_4$Ge$_4$ [12]. The absence of a visible anomaly in the easy plane susceptibility at $T_0$, despite a large mean field like anomaly in $C(T)$ and a weak anomaly in the susceptibility along the hard direction, is unusual for a pure magnetic ordering. Also the increase of $T_0$ for field along the easy direction is not expected for an antiferromagnetic transition in a three-dimensional system. In contrast, these results correspond to the behavior expected for quadrupolar ordering. As an example, our observations in YbRu$_2$Ge$_2$ are almost identical to those reported for TmAu$_2$ [13], where the upper transition was revealed to be ferroquadrupolar ordering. The behavior we observe at $T_0$ and the similarities with TmAu$_2$ strongly suggest that the transition at $T_0$ in YbRu$_2$Ge$_2$ corresponds to quadrupolar ordering [14]. While for some of the rare earth quadrupolar ordering is quite common, it is rather exceptional among intermetallic Yb compounds. The only well established example is YbSb [15], which shows a mixed type AFQ at 5.0 K. A quadrupolar ordering has recently be suggested to occur in YbAl$_3$C$_3$ [16], but this claim remains speculative because of an extremely large quadrupolar transition temperature $T_Q = 80$ K, exceeding all previously reported quadrupolar ordering temperatures by a factor of two, and the hexagonal symmetry of the structure, which should lead to a doublet CEF ground state and thus be rather unfavorable for quadrupolar ordering. Thus YbRu$_2$Ge$_2$
likely presents a unique type of ordering among Yb-compounds. Our results might also have some consequences for the interpretation of the unusual properties of YbRh$_2$Si$_2$.

In summary, we have grown single crystals of YbRu$_2$Ge$_2$ and investigated the physical properties of this compound by means of susceptibility, specific heat and resistivity measurements. The susceptibility is strongly anisotropic, being much larger for field in the basal plane than along the c direction. For field along the easy plane $\chi_{ab}(T)$ follows a Curie-Weiss law with an effective moment close to the value for free Yb$^{3+}$, while for field along the hard direction the curve $1/\chi_c(T)$ versus T shows a strong negative curvature indicating a large overall CEF splitting. The temperature dependence of the resistivity follows a standard metallic behavior above 50 K and shows a weak Kondo type increase below 50 K. At lower temperatures, anomalies in C(T), $\rho(T)$ and $\chi(T)$ evidence three successive phase transitions at $T_0 = 10.2$ K, $T_1 = 6.5$ K and $T_2 = 5.7$ K, $T_0$ being larger than the highest Yb-magnetic ordering temperature observed up to now in intermetallic Yb compounds. Just above $T_0$, the magnetic entropy calculated from the specific heat reaches almost Rln4 instead of Rln2 expected from the CEF ground state doublet. The large anisotropy of the susceptibility, the Curie Weiss behavior of $\chi(T)$ along the easy plane, the large magnetic entropy collected at low temperatures and the weakness of the Kondo like increase in $\rho(T)$ demonstrate that Yb is in a stable trivalent state. $S(T \geq T_0) \approx R \ln 4$ proves that the energy of the first CEF excited doublet is lower than 10 K, leading to a quasiquartet CEF ground state, a unique situation among YbT$_2$X$_2$ compounds. The shape of the anomalies at $T_0$ in $\chi(T)$ and its behavior in a magnetic field are unusual for magnetic ordering, but very similar to those reported at the ferroquadrupolar ordering in TmAu$_2$. In view of the quasiquartet CEF ground state, this strongly suggests the transition at $T_0$ to be quadrupolar ordering. In contrast, the strong decrease of $\chi(T)$ at $T_1$ indicates antiferromagnetic ordering, while the transition $T_2$ is likely related to a change in the magnetic structure. The combination of a quasiquartet CEF ground state, a high ordering temperature and the likely relevance of quadrupolar interactions makes YbRu$_2$Ge$_2$ a very interesting system among Yb-based compounds. Neutron diffraction and muSR experiments are now in progress in order to reveal the nature of the different transitions.

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