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Quasiquartet crystal-electric-field ground state with possible quadrupolar ordering in the tetragonal compound $YbRu_2Ge_2$

H. S. Jeevan* and C. Geibel
Max Planck Institute for Chemical Physic of Solids, Nöthnitzer Strasse 40, D 01187 Dresden, Germany

Z. Hossain
Department of Physics, Indian Institute of Technology, Kanpur 208016, India
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We have investigated the magnetic properties of $YbRu_2Ge_2$ 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. 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 suggests 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 $YbRu_2Ge_2$ 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 nonmagnetic state by changing the chemical composition or by applying pressure. At the crossover from the nonmagnetic to the magnetic state, one observes unusual properties such as 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_2X_2 compounds (T=transition metals, X=Si and Ge) crystallizing in the $ThCr_2Si_2$ or a related structure type, because some of these compounds are very close to this crossover. Two prominent examples are $CeRu_2Si_2$ (Refs. 1 and 2) and $CeRh_2Si_2$,[3] the former is just on the nonmagnetic side and shows an unconventional metamagnetic transition from a delocalized to a localized f state, while the latter 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_2X_2 compounds have now been thoroughly investigated, less study has been performed on the Yb-based homologues. For the Yb compounds with T=Ru, Os, Rh, Ir, only little or nothing is known about their physical properties. $YbRh_2Si_2$ (Refs. 4 and 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. An investigation of $YbIr_2Si_2$ (Ref. 6) has just been published: it is a heavy fermion system just on the nonmagnetic side of the critical point. Searching for further interesting Yb-based compounds, we synthesized $YbRu_2Ge_2$ and investigated its physical properties for more than structural data.[7] Our results revealed a stable trivalent Yb state, a rather complex ordering phenomena with three 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 that is unique among the YbT_2X_2 compounds. The behavior observed at T_0 suggest this transition to be a quadrupolar one, being a consequence of the quasiquartet crystal-electric-field (CEF) ground state. The combination of a quasiquartet CEF ground state, a high Yb ordering temperature, and the likely relevance of quadrupolar interactions makes $YbRu_2Ge_2$ 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] The x-ray-powder diffraction pattern of the polycrystals confirmed the $ThCr_2Si_2$ ($I4/mmm$) 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 patterns taken from crushed single crystals showed that some of the single crystals were single-phase $YbRu_2Ge_2$, 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.[7] 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 2–300 K and in an applied field from 1 to 5 T was measured in a commercial Quantum Design superconducting quantum interference device (SQUID) magnetometer (MPMS). The specific heat and the resistivity were determined in a commercial PPMS (Quantum Design) equipment using the relaxation method

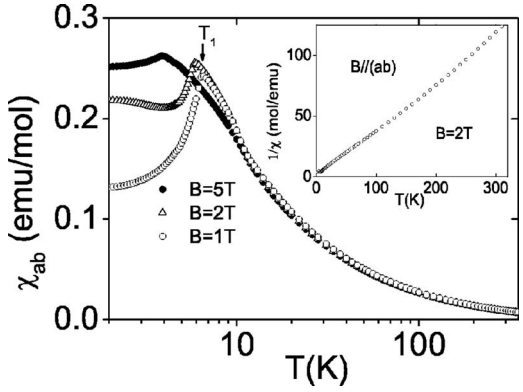

FIG. 1. Temperature dependence of magnetic susceptibility of $YbRu_2Ge_2$ for magnetic fields $B=1$, 2, and 5 T applied along basal plane. Inset: T dependence of $1/\chi_{ab}$ for $B=2$ T.

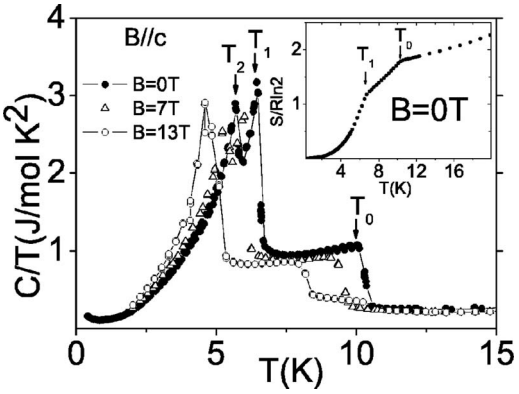

FIG. 3. Temperature dependence of the heat capacity of $YbRu_2Ge_2$, in a plot C/T vs T, for different fields applied along the c axis. The inset shows the temperature dependence of the entropy.

and a four-probe ac technique, respectively. All physical properties reported here were measured on the best single crystals that 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 evidence for a trivalent Yb state. $\chi(T)$ is strongly 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, χ_{ab} follows rather nicely a Curie-Weiss law from 20 K up to room temperature. The slight curvature in the $1/\chi_{ab}(T)$ vs 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, χ_c, is one order of magnitude lower than for field along the basal plane (Fig. 2). The $1/\chi_c(T)$ vs 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 $YbIr_2Si_2$ (Ref. 9) and $YbRh_2Si_2$,[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.

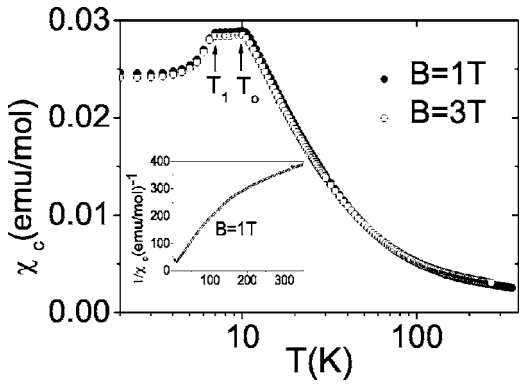

FIG. 2. Temperature dependence of magnetic susceptibility of $YbRu_2Ge_2$ for magnetic fields $B=1$ and 3 T applied along the c axis. Inset: T dependence of $1/\chi_c$ for $B=1$ T.

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 vs 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 λ-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 $4f$ hole that 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 toward 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 $\rho(300\text{ K})/\rho(2\text{ K})=22$ is an indicator for the good quality of the sample. The resistivity linearly decreases with temperature from room temperature down to 70 K and 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 $\rho(T)$ that 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 $\rho(T)$ increases further very strongly at $T_1=6.5$ K and only slightly more at $T_2=5.7$ K. 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

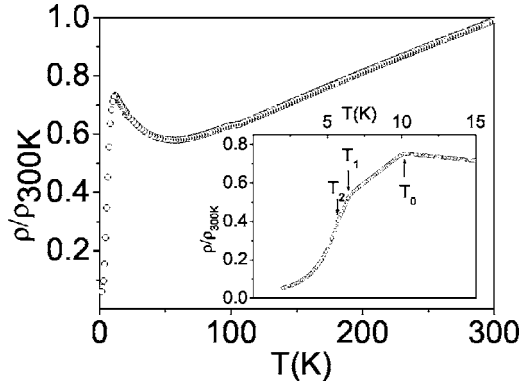

FIG. 4. Temperature dependence of the resistivity normalized to its value at 300 K. The inset shows $\rho(T)$ from 2–15 K. Kinks marked by arrows correspond to transitions at T_0, T_1, and T_2.

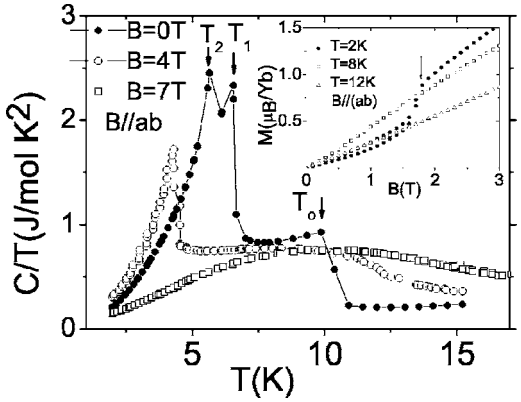

FIG. 5. This figure shows the strong dependence of the specific heat on field applied along the Basal plane in a plot C/T vs T for $B=0$, 4, 7 T. The inset shows the metamagnetic transition (arrow) at $B=1.8$ T observed in a magnetization M vs B plot at $T=2$ K for field along the basal plane.

range of the transitions, between 12 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 decrease 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 7 T (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 ΔM of only $0.5\mu_B$/Yb in the M vs 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 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 reveals only a broad, Schottky-like anomaly and no clear transition. The origin of this unusual behavior will be discussed below.

Except for the unusual behavior at T_0, $YbRu_2Ge_2$ 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 $LuRu_2Ge_2$ 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 nonmagnetic compound $LuRh_2Si_2$ at 12 K amounts to 0.17 J/mol K, less than 2% of the total entropy we determined for $YbRu_2Ge_2$ at the same temperature. In a tetragonal environment, the crystal field splits the $J=7/2$ state of Yb^{3+} 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 $R\ln 2$ slightly above T_N. Our surprising result is that the magnetic entropy of $YbRu_2Ge_2$ just above the highest transition T_0 is much larger, it almost reaches $R\ln 4$. This result, which was reproduced with different samples, proves that in $YbRu_2Ge_2$, 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,[11] and found that for the homologue and isoelectronic compound $YbRu_2Si_2$, a CEF calculation based on an extrapolation of the CEF scheme of other RRu_2Si_2 compounds (R=rare earth) postulated a small excitation energy (25 K) for the first excited CEF level. Our investigation reveals a very unusual quasiquartet CEF ground state in $YbRu_2Ge_2$, which is unique among YbT_2X_2 compounds.

With the presence of a quasiquartet CEF ground state, quadrupolar ordering becomes 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 $Yb_3Cu_4Ge_4$.[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 $YbRu_2Ge_2$ are almost identical to those reported for $TmAu_2$,[13] where the upper transition was revealed to be ferroquadrupolar ordering. The be-

havior we observe at T_0 and the similarities with $TmAu_2$ strongly suggest that the transition at T_0 in $YbRu_2Ge_2$ 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 $YbAl_3C_3$,[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 2, 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 $YbRu_2Ge_2$ 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 $YbRh_2Si_2$.

In summary, we have grown single crystals of $YbRu_2Ge_2$ 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 $1/\chi_c(T)$ vs 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 a very high Yb magnetic ordering temperature observed in intermetallic Yb compounds. Just above T_0, the magnetic entropy calculated from the specific heat reaches almost $R\ln 4$ instead of $R\ln 2$ 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. $S(T\geqslant T_0)\approx R\ln 4$ 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_2X_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 $YbRu_2Ge_2$ a very interesting system among Yb-based compounds. Neutron diffraction and μSR experiments are now in progress in order to reveal the nature of the different transitions.

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*Electronic address: jeevan@cpfs.mpg.de

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