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H-*T* phase diagram of URu_2Si_2 in high magnetic fields

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We have studied the ultrasonic velocity and ac susceptibility of URu_2Si_2 in magnetic fields up to 45 T. The resulting phase diagram reveals new phase boundaries that place strong constraints on theories of hidden order for this material. Furthermore, a significant difference between the constructed *H*-*T* phase diagram and that extracted from earlier pulsed field measurements is explained in terms of a large magnetocaloric effect. An offshoot of this analysis is that care should be taken in interpreting pulsed field measurements.

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The order parameter describing the 17.5-K transition in URu_2Si_2 is a subject of controversy despite 15 years of investigation. Early neutron and x-ray scattering measurements[1–5] indicated that antiferromagnetic order with a sublattice magnetization along the *c* axis was associated with the phase transition observed in the thermal, transport, and magnetic properties of URu_2Si_2.[6–11] However, the measured ordered moment was only $(0.03\pm0.01)\mu_B/U$, which is an order of magnitude too small to account for the observed change in entropy[7–10] associated with the phase transition. Furthermore, there has also been evidence that the antiferromagnetic phase is a minority phase, so that the true order parameter is unrelated to this phase.[12] These discrepancies have motivated a series of proposals for the order parameter (Refs. 13–16, and references therein). One recent proposal has generated great interest. Chandra, Coleman, and Mydosh have argued that experiments imply the existence of a novel orbital current state.[13] This orbital current state is similar to the *d*-charge density wave state discussed in the context of the high temperature superconducting cuprates.[17] Given the tentative nature of the proposal, it is important to identify the hidden order parameter in URu_2Si_2.

In addition to difficulties with understanding the hidden order, measurements of some important experimental properties are contradictory. Studies of the phase diagram of URu_2Si_2 fall naturally into two groups. In the first group pulsed magnetic fields up to 60 T were used.[18–24] In these experiments a series of nearly temperature-independent branches are seen in the region 35–40 T (Refs. 18 and 19) up to about 60 K. In Refs. 18–24 this transition was shown to be a *multistep* metamagnetic transition. In the second group dc magnetic fields were used.[6–8,11] Until quite recently these measurements have been restricted to a maximum field of about 25 T, and therefore to investigations of the hidden order transition only. Figure 1 shows the results of measurements from both groups; note the strong difference between the *H*-*T* phase diagrams extracted from the dc and pulsed field measurements. The dc field studies show a single phase boundary which persists down to zero field. This is an extension of the well-known zero-field transition, which occurs in URu_2Si_2 at about 17.5 K. On the other hand, the pulsed field investigations do not have any transition lines in common with the line emanating from ≈ 17 K observed in dc field measurements. The difference between pulsed field and dc phase diagrams was briefly mentioned in Refs. 6 and 18. In both papers the difference was attributed to a different origin for the high-field metamagnetic transitions and the hidden order transition. This explanation, together with the fact that the branch observed in dc fields is not seen in pulsed fields, is quite surprising.

In an effort to resolve this difference between the phase diagrams and to identify new physics in URu_2Si_2, we used the hybrid magnet at the National High Magnetic Field Laboratory in Tallahassee to study sound propagation (Fig. 2), ac susceptibility (Fig. 3), and the magnetocaloric effect[25] (Fig. 3) in magnetic fields up to 45 T and in the temperature range 1–20 K. The velocity of longitudinal sound propagated along the *c* axis (c_{33} mode) was measured at a frequency of 105 MHz; the field was applied along the *c* axis. Temperature measurements were done with a Cernox resistor: magnetoresistance corrections could introduce an absolute temperature shift of up to 0.5 K.

There are two main results of our study. The first result is a high-field phase diagram for URu_2Si_2 which is based mainly on the ultrasound measurements (see Fig. 4). This phase diagram is richer than any other found earlier, and places strong constraints on the nature of the hidden order. The second result is an explanation for the difference between the pulsed field phase diagram and the dc field phase diagram that we find here. In particular, we find that the large magnetocaloric effect is what leads to this difference (see Fig. 3).

High field phase diagram from ultrasound. We first discuss the ultrasonic results in detail. As one can see from Fig. 2, three steplike changes occur in the magnetic field dependence of the ultrasound velocity at a temperature of about 4.5 K. The position of the velocity steps coincides with the *H* values of the transitions measured in a pulsed field at this temperature.[18] By plotting the anomalies shown in Fig. 2, we extracted the *H*-*T* phase diagram presented in Fig. 4. Except for a hysteretic region which will be discussed next, we use the same symbols for the transitions extracted from up and down field sweeps, since they are essentially identical. For temperatures below 3.7 K, branch 2 splits into two branches

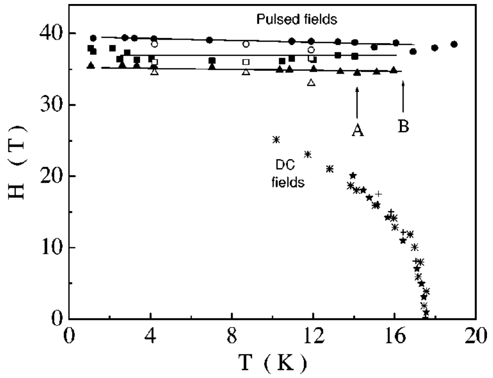

FIG. 1. H-T phase diagram of the metamagnetic transition in $\mathrm{URu_2Si_2}$ constructed from the measurements in dc magnetic fields:*, magnetoresistance (Ref. 6); +, specific heat (Ref. 7); ★, magnetization (Ref. 8); and from the measurements in pulsed magnetic fields: ▲, ■, ●, magnetization (Ref. 18); △, □, ○, ultrasound (Ref. 19, c_{11} mode). The lines are guides to the eye.

$2'$ and $2''$. Both low temperature branches show hysteresis. When the temperature reaches 1 K, the lower branch $2'$ joins with transition 1 (within the resolution of our measurements, which is $\cong 0.2$ T) and the hysteresis of this branch disappears. The higher branch $2''$ shows hysteresis in the temperature range 1–3.3 K. As the temperature falls the hysteresis loop expands along the magnetic field direction, but the velocity change does not depend on the temperature. To the best of our knowledge this hysteresis has not been observed previously. The existence of hysteresis allows us to identify transitions $2'$ and $2''$ as the first-order transitions.

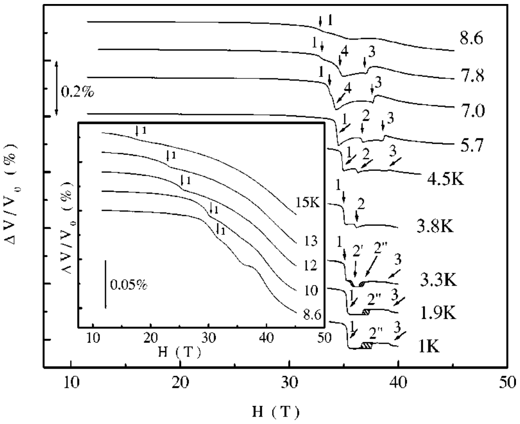

FIG. 2. Magnetic field dependence of ultrasound velocity in $\mathrm{URu_2Si_2}$ at different temperatures. The curves are shifted for clarity. The arrows indicate transitions. The hatched area shows the hysteresis region of transitions $2'$ and $2''$.

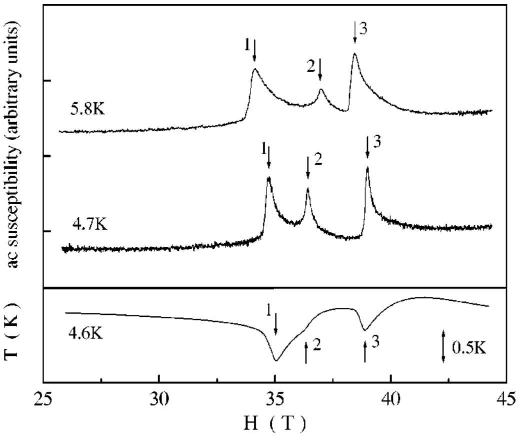

FIG. 3. Magnetic field dependence of the ac susceptibility at different temperatures. The lowest curve is the MCE trace (for increasing fields) starting at 4.6 K (Ref. 25).

The phase diagram shows a variety of phase lines and four critical points I–IV in Fig 4. Given the lack of hysteresis associated with all the phase transitions except for branches $2'$ and $2''$, it is tempting to associate the other phase boundaries with second order transitions. However, this is not allowed by thermodynamics. Of particular relevance to theories of hidden order is the low-temperature region of the hidden order phase transition: branch 1. Thermodynamics requires that, for $T<7$ K, the hidden order transition 1 be first order. This follows from two assumptions: (1) the hidden order transition for $T>7$ K is second order, and (2) three phase boundaries meet at the critical point I ($T=7$ K and $H=33$ T).[26] A definite determination of the order of the other phase transitions will require more measurements. In particular, the behavior of branch 4 at higher magnetic fields needs to be resolved. Above 10 K the behavior of branch 4 is unclear. It quickly becomes unobservable; however it is not clear whether this is associated with a small magnetoacoustic interaction at high temperatures or whether this branch moves above our upper field of 45 T. For this reason the accuracy of the branch 4 positions in this region is ≈ 1 T and is marked by the error bars in Fig. 4. All other branches, and branch 4 below 9 K, are measured with an accuracy ≈ 0.2 T, which is smaller than the symbol size in Fig. 4.

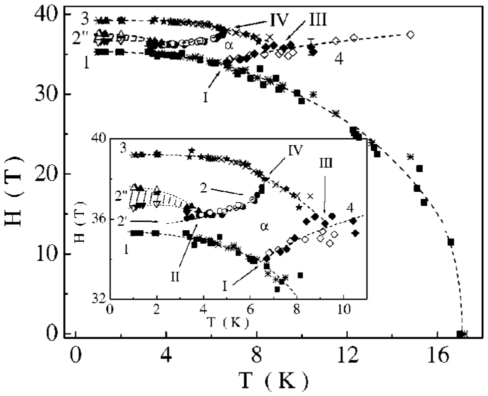

FIG. 4. H-T phase diagram of the $\mathrm{URu_2Si_2}$ metamagnetic transition extracted from ultrasonic (■, branch 1; ●, branches 2 and $2'$; ▲, branch $2''$, hysteresis region field sweeps up; ▼, branch $2''$, hysteresis region field sweep down; ★, branch 3; ◆, branch 4) and ac susceptibility measurements (*, branch 1; ○, branches 2 and $2'$; △, branch $2''$, hysteresis region field sweep up; ▽, branch $2''$, hysteresis region, field sweep down; ×, branch 3; ◇, branch 4) at continuous magnetic fields. Inset: High field/low temperature part of the same H-T diagram. The hatched area shows the hysteresis region. I–IV, critical points; α, the new phase.

The ac susceptibility measurements were somewhat peripheral in this study and limited data were taken. Nevertheless, the *H-T* phase diagram extracted from these measurements shows a behavior similar to that of the ultrasound for phase lines 1–4. In particular, the hysteresis of branch 2′ has been observed in ac susceptibility measurements as well.

The phase diagram of Fig. 4 has implications for the hidden order phase. Prior to discussing these implications we will give an overview of the current debate of the nature of the hidden order. The hidden order has been debated extensively over the last 15 years, and many proposals exist. From a symmetry point of view, these proposals fall into two classes that are tied to the relationship between the hidden order and the antiferromagnetism. In the first class, the hidden order has the same symmetry as the antiferromagnetism.[5,27] This has the disadvantage that recent muon spin resonance measurements indicate that the antiferromagnetic order is a *minority phase*.[15] For this reason, the second class now appears more promising. In this case, the hidden order has an unknown symmetry that is *different* from that of the antiferromagnetic state.[13,28,29] While there appears to be stronger support for the second class, there remains the difficulty that it appears that the antiferromagnetic order and the hidden order have the same transition temperature. This is not generally expected for two order parameters of different symmetry. The role the above phase diagram plays in understanding the hidden order depends on the nature of the phase boundary from the normal phase to phase α. If this transition is second order (so that the critical point I is a bicritical point), the implication is that a second hidden order parameter exists. A possible realization for such a scenario is an *orbital-flop* transition, though more work will be required to understand the origin of the other phase boundaries. However, if the normal to phase α phase transition 1 is first order then it is likely that the high-field phase transitions are metamagnetic transitions that are due to level crossings of the localized f states of the uranium ions. Such a scenario has been explored in Refs. 18 and 28.

Origin of the different pulsed field and dc field phase diagrams. Clearly, the *H-T* phase diagram, as measured by ultrasound in high dc fields, is different than that determined with pulsed fields. The dc field phase diagram constructed above shows that transition 1, previously identified as a lowest step of the metamagnetic transition (which occurs in URu_2Si_2 at 35.3 T in the pulsed field experiments at low temperatures), and the hidden order transition (which is observed at 17 K in zero magnetic field) are two manifestations of the *same* transition. This result differs from the conclusion arrived at in Refs. 6 and 18, that the transitions observed in the pulsed and dc fields had a different origin. We suggest that this phase boundary is not seen in the pulsed field experiments due to the strong *magnetocaloric effect* (MCE), recently observed in URu_2Si_2 (Refs. 25 and 30): a large cooling of the sample in traversing up in field through transition 1. The normal magnetocaloric effect in a paramagnet is an *increase* in temperature because of the magnetic field's tendency to order the spins and thereby lower the entropy. In this metal the opposite happens; the temperature *decreases*, implying there is an increase in entropy. Figure 3 shows a trace of the magnetocaloric effect. The temperature of the sample is measured with a Si specific heat calorimeter, as the field is swept in the hybrid magnet at a rate of 2 T/min. In the presence of such a temperature shift the actual temperature of the URu_2Si_2 sample at the transition is *lower* than the initial temperature of the helium bath (and the sample). As a result, the apparent temperature independence of the phase diagram branches measured in pulsed magnetic fields is an artifact.

It is natural to assume that point A in the pulsed field *H-T* diagram (see Fig. 1), where the metamagnetic transition evolves from three steps to two steps, and point B (Fig. 1), where the two steps merge into one, coincide to points II and III of the diagram shown in Fig. 4. In this way we can estimate the temperature change that likely occurred during the experiments in Ref. 18, for which we find 7 K. We consider this value reasonable as compared to the 1-K change of temperature observed during the much slower sweep rate measurements in a dc magnetic field (see Fig. 3). Of course, below 4.2 K, where the sample is surrounded by liquid helium (or below 1.7 K if the sample is placed in a He^3 chamber), the temperature changes in the sample will be much smaller, which is why our 1–4.2 K results agree well with the results of Ref. 18 at 1.3–4.2 K.

It is important to note that the phase diagram determined here is, on the whole, similar to that measured using the MCE on the *same* sample as well as on another sample.[25,30] The higher sensitivity of the ultrasonic technique, the smaller temperature intervals between field sweeps, and the opportunity to work below 3 K, have yielded important new details of the phase diagram compared to the results obtained in Refs. 25 and 30. Nevertheless in Fig. 3 of Refs. 25 and 30 one can see a hint of the fourth branch in the region 6–7 K. When this paper was being prepared for publication a phase diagram similar to that observed in Refs. 25 and 30 was published.[31]

In conclusion, the well-known transition which occurs in URu_2Si_2 in zero magnetic field at 17 K was observed down to 1 K. The field of the transition increases to 35.3 T as the temperature decreases. Other phase boundaries were observed below 9 K in the magnetic field region 36–40 T. Hysteresis observed at low temperature for the middle transition (at about 37 T) implies a first order transition.

Along with the discovery of new phases in URu_2Si_2, two additional phenomena were uncovered in the present work. First, a maximum appears at 29 T in the magnetic field dependence of the ultrasonic velocity, for which there is no explanation at present. We assume that this maximum, and the maxima observed in the magnetoresistance[21] and Hall coefficient[22] at 29 T, have the same yet-unknown origin. Second, the behavior of velocity at the 39-T transition is very unusual: at temperatures above about 4 K the velocity decreases discontinuously as the magnetic field rises; at 4 K there is no evidence of a transition; and below 4 K the velocity increases discontinuously. We assume that such a velocity change is not associated with lattice properties of URu_2Si_2, but more likely relates to an ordering of the electronic system or to a spin density wave state, for example.

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