Heat capacity and magnetic phase diagram of the hydride CeRuSiH

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Abstract. The hydride CeRuSiH exhibits antiferromagnetic order with two transitions at $T_{N1} = 7.5$ and $T_{N2} = 3.1$ K. Furthermore, magnetization measurements $M(H)$ up to $H = 45$ kOe shows a metamagnetic double transition at low temperatures, suggesting a complex magnetic phase diagram. Here, we present magnetization measurements and heat capacity data up to 90 kOe, which allows us to complete the magnetic phase diagram. In addition, from the analysis of the heat capacity, we propose a model for the crystal field splitting.

1. Introduction

Among the rare earth intermetallic, the Ce based one are characterized for having a strong dependence of their magnetic properties on the interatomic distance. In this sense, many studies have been performed using chemical substitution and/or hydrostatic pressure. Another important way to modify the atomic volume and then the magnetic interactions is hydrogen absorption [1, 2]. Recent hydrogenation studies on the non-magnetic heavy fermion ternary silicide CeRuSi, have discovered that CeRuSiH exhibits antiferromagnetic order with two transitions at $T_{N1} = 7.5$ and $T_{N2} = 3.1$ K [3]. In addition, magnetization measurements $M(H)$ up to $H = 45$ kOe revealed a metamagnetic double transition at low temperatures, suggesting a complex magnetic phase diagram [3]. Neutron powder diffraction experiments evidenced an incommensurate magnetic structure below $T_{N1}$ that transforms into a commensurate one at $T_{N2}$ [4]. Also, the influence of pressure on the magnetic properties of CeRuSiH has also been analyzed up to 10 kbar [5], confirming that the increase of the unit cell volume in the sequence CeRuSi → CeRuSiH is the main responsible of the induced antiferromagnetic order in the hydride. Now, we present a detailed investigation of the $M(T)$ and $M(H)$ measurements up to $H = 90$ kOe. In addition, we report on the magnetic field dependence of the heat capacity of CeRuSiH. These new results confirm the previous picture obtained up to $H = 45$ kOe, allowing us to extend the $(H, T)$ magnetic phase diagram up to 90 kOe.

2. Experimental details

A polycrystalline CeRuSi sample was heated at 523 K under vacuum for 12 hours and then exposed for 2 days under 4 MPa of hydrogen gas at the same temperature. More details of sample preparation can be found in reference [3]. Magnetization measurements have been performed in a PPMS system in magnetic fields up to 90 kOe. Heat capacity measurements were carried...
out by a relaxation method, also using the PPMS system. The sample was a plate of 0.4 mm thickness and 7 mg weight, obtained by compressing the original powder.

3. Results and discussion
Susceptibility curves, measured cooling the sample in the presence of applied magnetic fields, are depicted in Figure 1. Below 40 kOe, all the curves shows a maximum around $T_{N1} = 7.5$ K. When the temperature decreases, the behavior changes with applied field, defined a second transition at lower temperatures in excellent agreement with reference [3], in which a detailed analysis of this low field range can be found. At 50 kOe, the susceptibility shows a broad maximum centred at 5 K. At higher fields, the maximum disappears, and the susceptibility tends to saturate when the temperature decreases, approaching to the behavior expected in ferromagnetic material. In this field range ($H \geq 50$ kOe), the transition temperature has been defined at the inflexion point of $\chi(T)$ (temperature at which the $d\chi/dT$ curve exhibits a minimum).

The magnetic field dependence of the isothermal magnetization, displayed in Figure 2, has been measured first increasing the field up to 90 kOe and then, decreasing the field down to 0 kOe. At $T = 2$ K, the curve shows two metamagnetic transitions at $H_{C1} = 6.7$ kOe and $H_{C2} = 48$ kOe. When the temperature increases, $H_{C1}$ shifts to higher fields, whereas $H_{C2}$ moves in opposite direction. This tendency is followed up to $T = 7$ K, where the two transitions join at $H_C \approx 30$ kOe. At the critical field $H_{C1}$ the magnetization exhibit a clear irreversibility, which is better observed in the inset of Figure 2. At $T = 2$ K, the irreversibility has a field width of $\Delta H_{C1} \approx 0.6$ kOe; this value remains nearly constant below 7 K.

The heat capacity ($C_p$) measured at zero magnetic field between 2 and 300 K is shown in Figure 3. The increase of the $C_p$ above the magnetic transition is due to the electronic and mainly phonon contributions. In addition, we should have a crystal field contribution. In the tetragonal symmetry of CeRuSiH, it is expected that the sixfold degenerated 4f state of Ce$^{3+}$ ions split into three doublets, with the excited stated separated from the ground state by energy

![Figure 1](image1.png)

**Figure 1.** Temperature dependence of the susceptibility of CeRuSiH measured under different applied fields.

![Figure 2](image2.png)

**Figure 2.** Field dependence of the magnetization of CeRuSiH measured at different temperatures. The inset shows an enlargement around the first metamagnetic transition.
gaps $\Delta_1$ and $\Delta_2$. In order to determine the ground multiplet, the experimental data was fitted to the addition of these three contributions. In particular, for the phonon contribution, due to the absence of an isomorphous non magnetic compound, and the important different weight of the constituents, we use a Debye model assuming the existence of two Debye temperatures: $\text{Cph} = n_1 \text{Cph} (\Theta_{D1}) + n_2 \text{Cph} (\Theta_{D2})$ where $n_1 + n_2 = 4$ was fixed. Furthermore, we use an electronic coefficient $\gamma = 26 \text{ mJ/molK}^2$ which was obtained from the low temperature analysis [3]. More details about this procedure can be found in reference [6], where a similar method was successfully used in CeNiGaH$_{2.1}$. The best fitting corresponds to $n_1 = 2.9$, $\Theta_{D1} = 358 \text{ K}$, $\Theta_{D2} = 2300 \text{ K}$, $\Delta_1 = 127.2 \text{ K}$ and $\Delta_2 = 127.8 \text{ K}$. The energy of the crystal field splitting is in good agreement with the values suggested from of resistivity measurements [3]. The high value of $\Theta_{D2}$ could be attributed to the high energy phonon spectra associated to the light H atoms, which are the main responsible of the feature that the experimental data still have an important slope at 300 K. In the inset of Figure 3 it is depicted the magnetic contribution obtained as $C_{\text{mag}} =$
Cp - C\textsubscript{pho} - C\textsubscript{el} - C\textsubscript{CEF}; the peak and its shoulder at lower temperatures define clearly the two magnetic transitions at \(T_N1 = 7.5\) and \(T_N2 = 3.5\) K respectively, in agreement with the previous results.

The effect of the magnetic field on the heat capacity, depicted in Figure 4, provide us a valuable information about the magnetic phase diagram, and in particular on its extension up to 90 kOe. In Figure 4a it is observed that when the field starts to increase, the peak shifts to lower temperatures, as it is expected in antiferromagnetic compounds. Moreover, the low temperature shoulder shifts to higher temperatures, as is indicated by arrows for some selected fields. Above 28 kOe, Figure 4b, the most significant features are i) the two transitions collapse and ii) the peak becomes narrow and its height increases. The last one is quite important, because usually the effects of magnetic field on Cp is the opposite: the peak broadens and decreases in height. The unusual field dependence found in CeRuSiH is related with the incommensurate magnetic structure, which evolves towards commensurate one with field. Therefore, for the magnetic field corresponding to the maximum height (\(H = 33\) kOe), it is expected that the system is directly ordered from the paramagnetic state into a commensurate magnetic structure. At \(H = 45\) kOe, Figure 4c, a small bump appears around 7.4 K and then, by decreasing the temperature, emerges a peak surrounded by two shoulders. By increasing the magnetic field, this multi-structured peak becomes less intense whereas the bump at 7.4 K transforms into a maximum at 90 kOe.

Using all the previous data, it is possible to put forward the magnetic phase diagram shown in Figure 5. Below 45 kOe, the new data coincide with the previous one (blue lines) [3], in which phases (I) and (II) correspond to antiferromagnetic arrangement, whereas phase (III) shows a ferrimagnetic character. The new information obtained in this paper is represented in red. First, it is observed that the increase of the critical filed \(H_{C2}\) by decreasing the temperature, tends to saturate at about 50 kOe. Second, between the paramagnetic and the ferromagnetic phase (IV) there are three intermediate phases, probably of ferrimagnetic nature. These phases, although give rise to a broad increase of the magnetization in the M(T) curves, are clearly detected in the heat capacity. This phase diagram resembles those found in other Ce intermetallics as CeRu\textsubscript{2}(Si\textsubscript{1-x}Ge\textsubscript{x})\textsubscript{2} [7] or Ce\textsubscript{0.8}La\textsubscript{0.2}Ru\textsubscript{2}Si\textsubscript{2} [8]. In these alloys, the antiferromagnetic order is induced by the expansion of the lattice due to the substitution of a small amount of Ge for Si or La for Ce respectively, and in both cases, the magnetic structure is also incommensurate.

Summarizing, \(\chi(T)\), M(H) and Cp data up to 90 kOe allowed us to complete the complex magnetic phase diagram of CeRuSiH, in which the incommensurate magnetic structure evolves towards a commensurate order by increasing the magnetic field. Furthermore, from the analysis of the Cp between 2 and 300 K, a crystal field splitting is proposed.

This work was financially supported by the European Science Foundation (ECOMCOST action P16) and by the Spanish Project MAT2008-06542-C04

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