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To cite this article: Steffen Hartwig et al 2015 *J. Phys.: Conf. Ser.* **592** 012091

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Magnetic neutron diffraction and pressure studies on CeRuSn

Steffen Hartwig and Karel Prokeš

Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner Platz 1, M-AQM, 14109 Berlin, Germany

Yingkai Huang

Van der Waals-Zeeman Institute, University of Amsterdam, 1018XE Amsterdam, The Netherlands

Rainer Pöttgen

Institut für Anorganische und Analytische Chemie, Westfälische-Wilhelms-Universität Münster, 48149 Münster, Germany

E-mail: `steffen.hartwig@helmholtz-berlin.de`

Abstract. We have determined the influence of magnetic fields on the crystal and magnetic structures of CeRuSn using single crystal neutron diffraction and susceptibility measurements at various pressures up to 7.4 kbar and temperatures down to 1.6 K. CeRuSn adopts below 160 K an incommensurately modulated crystal structure. It orders antiferromagnetically below T_N=2.8 K in an incommensurate manner as well. This Néel-temperature is pressure independent up to 7.4 kbar. The neutron diffraction experiments detected a magnetic modulation vector $q_{mag} = (0, 0, 0.175)$, however, it is commensurate with the incommensurate crystal structure with $q_{nuc} = (0, 0, 0.35)$. At 0.6 T as well as at 0.9 T metamagnetic transitions have been observed via magnetic property measurements. The magnetic field of 0.9 T applied along the c-axis suppresses the magnetic reflections. The moments align ferromagnetically along the modulated crystal structure. Up to 3 T no change of the wavelength of the crystal structure modulations could be detected.

1. Introduction

Lately, the investigation of aperiodic (incommensurate) crystal structures has grown in interest. New methods of analyzing data give the possibility to revisit supposed established results and to discover effects in new materials, like CeRuSn. This intermetallic compound possesses a large variety of exceptional yet non fully understood structural, electronic and magnetic features. The crystal structure of CeRuSn is found to be aperiodic in multiple manners[1] and can now be characterized, since recent improvements of the JANA2006-program [2] allow an investigation of materials which are incommensurately modulated in both crystal and magnetic structures.

At ambient conditions CeRuSn adopts a CeCoAl-related crystal structure (1c-structure)[3], which possesses the space group C2/m, the cell parameters a=11.55 $\mathring{A}$, b=4.75 $\mathring{A}$, c=5.11 $\mathring{A}$ and β=102.975° at 1.6 K.[1][3] However, CeRuSn exhibits at room temperature two different

Cerium sites unlike CeCoAl differing in their valence states (Ce^{3+} versus an intermediate $Ce^{4-\delta}$), which leads to a doubling of the c-axis parameter (2c-structure).[3][4][5] Slightly beneath room temperature, between 290 K and 160 K, the material undergoes a hysteretic structural phase transition becoming incommensurately modulated along the c-axis. After some initial temperature dependence the modulation wave vector eventually locks in at $q_{nuc} = (0, 0, 0.35)$ at low temperatures. This is visible in unusual high atomic displacement factors in the pair distribution function [6] as well as directly by neutron diffraction.[1] The atomic positions are sinusoidally modified in their x and z components and adopt the superspacegroup C2/m.1'(a0g)0ss. CeRuSn shows also a highly anisotropic magnetic behaviour and orders antiferromagnetically below T_N=2.8 K. Additionally, neutron single crystal diffraction shows, that the magnetic structure is modulated with the magnetic modulation vector $q_{mag} = 1/2$ q_{nuc}. The magnetic moments of the Ce-ions, which are confined to the a-c-plane, appear to be almost collinear. However, the size of the moments varies with the modulation along the c-axis. Furthermore an unusual connection between magnetic moment and atomic distances has been discovered. The phase shift between both modulations leads to unusual high valence bond sum at positions with small ionic distances.[1]

Since the structural transition is accompanied by yet not understood modifications of Ce-valence at different sites[5][7][8], the interplay between structure, magnetism and valence in CeRuSn appears to be an interesting field for investigations. This paper shall help to clarify the influence of magnetic fields on these incommensurate modulations.

2. Sample preparation

A large single crystal of CeRuSn has been grown using a modified tri-arc Czoralski technique in a continuously Ti-gettered ultrapure Argon atmosphere from a stoichiometric melt of the constituent elements. The quality of the sample has been checked and the crystal has been oriented via x-ray Laue backscattering method.[1]

3. Techniques

The neutron single-crystal diffraction experiments have been performed at the BER II neutron source of the Helmholtz-Zentrum Berlin on the instrument E4 using a 4T horizontal magnet. This instrument is a single crystal diffractometer with an area detector. During this measurements a monochromatic beam with $2.478 \mathring{A}$ was used. The magnetic field was applied in the scattering plane along the easy c-axis. Since CeRuSn shows an anisotropic magnetic behaviour (Fig. 1), this minimizes the effects of stress. Additionally, the sample was only wrapped in aluminum foil for holding the sample in the cryostat instead of other kinds of mechanical fixation or gluing. Data have been reduced with the Large Array Manipulation Program.[9] For data refinement the program Jana2006 was used.[2]

Magnetic susceptibility measurements have been taken using a Quantum Design 5T Magnetical properties measurement system SQUID.

For pressure studies a clamped-type CuBe pressure cell was used with Daphne oil as pressure transmitting medium. To determine the pressure at low temperatures the pressure-dependent superconducting transition temperature of a small piece of high quality lead with known superconducting properties was measured with the remanent field of the superconducting coil. The sample in the pressure cell was oriented with its c-axis parallel to the magnetic field of the SQUID-magnetometer.

4. Magnetic bulk measurements

Previous susceptibility measurements at low temperatures reveal an antiferromagnetic transition at T_N=2.8 K.[1] This transition temperature shifts with an applied field to lower values.[10] A significant anisotropy of the magnetic susceptibility has been discovered. Highest susceptibility
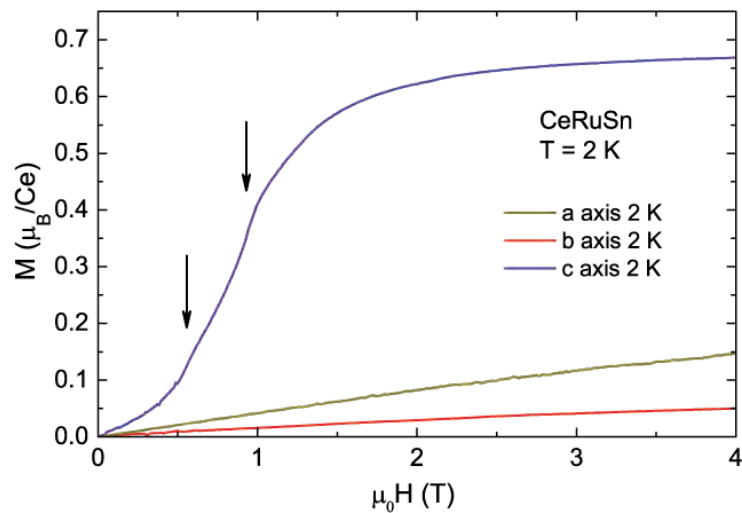
Figure 1. The magnetic field dependence of the magnetization of CeRuSn measured at 2 K for the three principal directions is shown up to 4 T. Strong magnetic anisotropy, especially along the c-axis, can be seen. The arrows mark metamagnetic transitions at 0.6T and 0.9T, which is equivalent to the results of neutron measurements.[1]
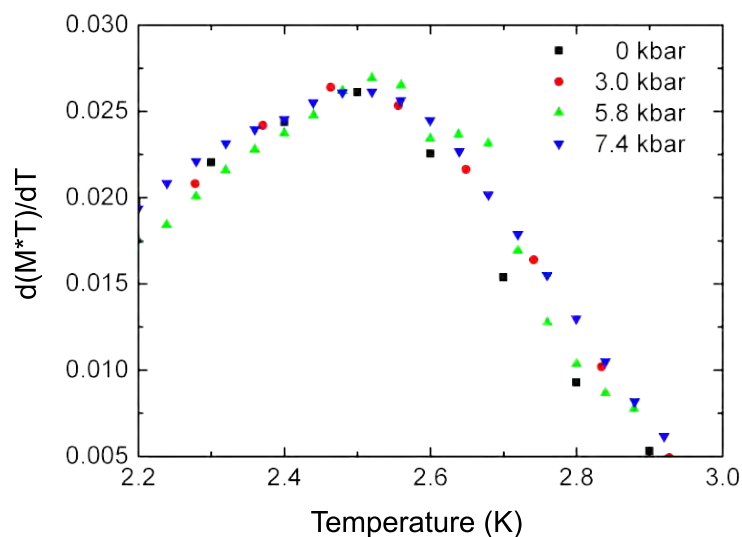

Figure 2. The temperature dependence of $\frac{\partial}{\partial T} M(T) \cdot T$ of CeRuSn obtained by SQUID-measurements with an CuBe pressure cell at 1000 Oe applied along the c-axis. A shift of the Néel-temperature has not been observed. Slight difference of line-shape can be explained by the influence of the changed distance to the pressurizing clamps and seals of the cell.

is found at the c-axis, while the b-axis represent the magnetic hard axis. Magnetization measurements at 2 K additionally show two metamagnetic transitions at fields of 0.6 T and 0.9 T. This documents a collapse of the antiferromagnetic order.

Our measurements under pressure with an applied field of 1000 Oe revealed that the Néel-temperature remains practically constant up to the highest applied pressure of 7.4 kbar. This result is somewhat surprising regarding the sensitivity of the samples properties to changes of the unit cell volume. For example one possible explanation of the incommensurate phase transition and the sudden reduction of the c-axis parameter is the Ce-based Kondo collapse scenario.[4][7][11] The Néel-temperature has been determined by calculating the maximum of the derivation $\frac{\partial}{\partial T}\left(M\left(T\right)\cdot T\right)$ resulting in T_N=2.5 K for all pressures, which actually deviates significantly from previous bulk measurements on the same crystal. One possibility to explain the disagreement is a large heat capacity of the pressure cell leads to a temperature delay between sensor and sample while heating. Since the heating velocity was constant for all the measurements this does not mask a change of T_N. Measurements under pressure in higher magnetic fields up to 5 T show only minor variations of the saturation moment of CeRuSn.

5. Neutron diffraction

The fact that magnetic reflections are described by a propagation vector with the only component along the easy magnetic c-axis requires a use of a horizontal field magnet that restricts the number of visible reflections enormously. In total, the temperature and magnetic field dependencies of only five different reflections could be measured. Those contain main structural reflections of the CeCoAl type, structural incommensurate satellites and antiferromagnetic reflections. Fig. 4 shows the integrated intensities of some of these reflections as a function of an applied field at 1.6 K.

Several antiferromagnetic reflections appear below T_N at incommensurate positions, indexable with the modulation vector $q_{mag} = (0, 0, 0.175)$ (Fig. 3). With increasing magnetic field at 1.7 K the intensity of the magnetic reflection (1, 0, 0.175) (see Fig. 4) decreases, make a short plateau between ≈0.3 and 0.6 T and finally vanishes at 0.9 T. This field is equivalent to the metamagnetic transition shown before in Fig.1, which indicates a loss of magnetic order in the macroscopic properties. Simultaneously, the intensities of the main structural peaks increase promptly in this region and stays constant above 0.9 T.

The intensity of the structural satellites from the modulated crystal structure with $q_{nuc} = (0, 0, 0.35)$ remains nearly unaffected by a magnetic field up to 3 T. A shift of the magnetic or structural reflection due to the magnetic field could not be detected (Fig. 3).

The intensities of the obtained reflections were used for a data refinement based on the CeCoAl-like 1c-structure. Since the system behaves ferromagnetic at 3 T, every Ce-atom was for simplicity assumed to be equally magnetic in its Ce^{3+} state. In this way the refinement with the average structure without modulations can be directly compared with the magnetic moments obtained by refinements with Ce atoms modulated in position and valence at low temperatures.[1][7] The refinement of the magnetic moment at the Cerium positions for this average structure converges to 0.46 μ_B/Ce at 3 T (4 reflections used, 1 parameter refined, agreement factor R=7.5). Previous magnetization measurements shown in Fig. 1 indicate a magnetic moment of approximately 0.66 μ_B/Ce along the c-axis close to the saturation moment and therefore ≈40% larger. We note that the use of the average structure is certainly not correct and the rather small number of reflections increases the error.

If one uses the modulated setting, obtained by earlier neutron diffraction experiments, different results occur. Ferromagnetic moments along the c-axis modulated with the same wavelength as the structure lead to an magnetic moment between 0.03 and 0.796 μ_B/Ce. However, these results have to be handled carefully, since the number of reflections is equal to the number of refined parameters.
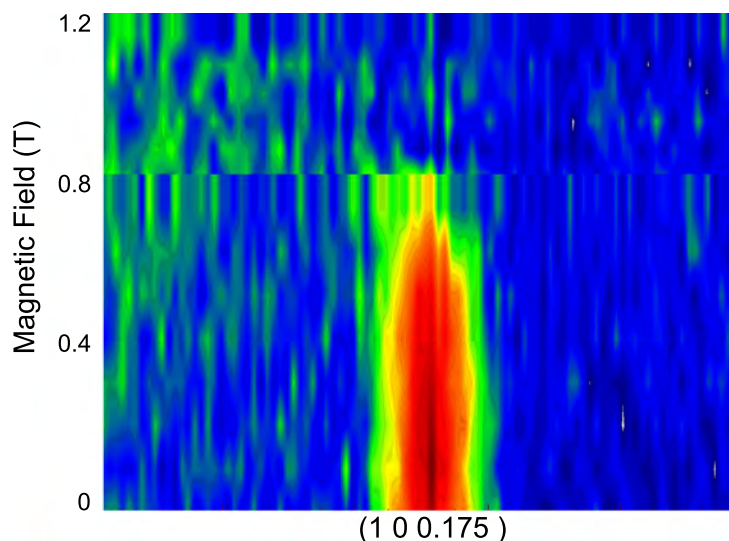
Figure 3. Field dependence of the antiferromagnetic (1 0 0.175) reflection with an magnetic field applied along the c-axis. The reflection vanishes at higher magnetic fields. A ferromagnetic alignment occurs. A shifting of the reflections position with increasing field is not visible.

In order to be able to disclose more details of the field-induced ferromagnetic state in CeRuSn, another neutron diffraction experiment with shorter wavelength is needed.

6. Conclusion

In conclusion, we have shown that the crystal structure is not affected by a magnetic field of 3 T. The macroscopic magnetic properties mirror the microscopic behaviour of CeRuSn, which we have investigated via neutron diffraction. At low temperature and low fields neutron diffraction data show antiferromagnetic peaks at incommensurate positions. These disappear at the metamagnetic transition around 0.9 T, while the intensity of the main structural peaks is increasing, which indicates a ferromagnetic alignment.

There is no pressure dependence neither of the Néel-temperature nor of the saturation moment up to 7.4 kbar. The antiferromagnetic order of CeRuSn thus turned out to be surprisingly stable in consideration of the relationship between magnetic moment and Ce-Ru distance.[3][7] Of course, this pressure is comparable low and a more distinct variation of the Néel-temperature at higher pressures is expected. Especially the application of high uniaxial pressure along the c-axis, thus along incommensurate modulation vectors q_{nuc} and q_{mag}, is very likely to have a significant effect on the arrangement of the magnetic spins in CeRuSn and is consequently an interesting task for further investigations.

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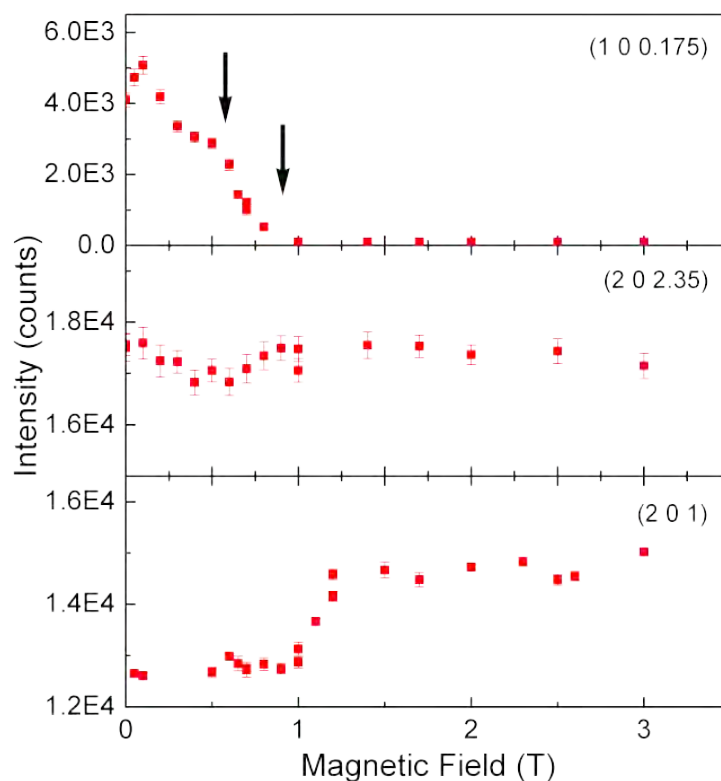[6] Prokeš K, Kimber S A J, Mydosh J A and Pöttgen R 2014 *Phys. Rev. B* **89**(6) 064106

Figure 4. Integrated intensities of selected reflections at 1.7 K versus magnetic field along the easy c-axis. (1 0 0.175) represents a magnetic reflection. (2 0 2.35) is a satellite of of the modulated crystal structure. At 0.9 T the magnetic reflection vanishes. This correlates with the second metamagnetic transition shown in Fig. 1. Simultaneously the intensity of the structural peak (2 0 1) increases and saturates abruptly. Arrows mark the metamagnetic transitions deduced from bulk measurements.

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