

Antiferromagnetic ordering in a mixed-valent cerium compound CeRuSn

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We report the results of extensive neutron powder diffraction experiments on a ternary compound CeRuSn in a temperature range from 2 to 520 K. At room temperature CeRuSn orders in a monoclinic structure that is related to the CeCoAl type by the doubling of the c -axis parameter caused by the splitting of the original single sites for each element into two sites. Upon cooling a very broad hysteretic structural transition has been observed in CeRuSn leading to the presence of higher-ordered variants having multiple c -axis parameters. Depending on the temperatures, one or the other variant seems to be more stable, but the sample as a whole becomes multiphase. We find also evidence for further symmetry lowering at low temperatures. CeRuSn is found to exhibit an antiferromagnetic order below $T_N = 2.8(1)$ K. The order is described by two incommensurate propagation vectors $q_1 = (0, 0, \approx 0.30)$ and $q_2 = (0, 0, \approx 0.43)$ with respect to the doubled crystal structure variant. Although the details of the magnetic structure remain elusive, the best agreement has been found for a complicated distorted cycloidal magnetic structure with Ce moments of $\approx 0.7 \mu_B$ being confined to the ac plane.

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I. INTRODUCTION

Intermetallic compounds based on cerium have been long studied for their correlated electron behavior exhibiting valence fluctuations, hybridization gapping, and Kondo-lattice antiferromagnetism (AF).¹⁻³ Recently discovered equiatomic Ce-based stannide CeRuSn possesses remarkable structural, electronic, and magnetic features⁴⁻⁶ that are not yet fully understood. Above room temperature, CeRuSn adopts a superstructure of a monoclinic CeCoAl crystal structure⁴ by a doubling along the c axis leading to the splitting of originally single Ce, Ru, and Sn crystallographic positions into two independent Wyckoff sites. This modification seems to be stable up to at least to 800 K (Ref. 7). The two resulting Ce sites have a distinct coordination that was confirmed also by ¹¹⁹Sn Mössbauer spectroscopy.⁸ The Ce1 sites are characterized by unusually short Ce–Ru bonds of 233 pm that are below the sum of the covalent Ce and Ru radii.⁴ A detailed structural analysis, bulk magnetic measurements, and band-structure calculations suggest that Ce ions residing in the two inequivalent sites are in different valence states, namely intermediate-valence Ce^{(4-δ)+} (Ce1) and trivalent Ce³⁺ (Ce2) states.⁴⁻⁶ The Curie constant determined from the magnetic susceptibility measurements at temperatures above room temperature is reported to be compatible with only 50% Ce ions being in the Ce³⁺ state.⁵ The existence of two different Ce valence states seems to be, at first glance, improbable for a metallic system, however, band-structure calculations confirm this conclusion and predict a magnetic instability associated with the Ce2 site at low temperatures.⁶ Indeed, previous magnetic bulk measurements suggest an AF order below $T_N = 2.7$ K (Ref. 5). It is the aim of this paper to determine its main crystallographic and magnetic characteristics via neutron powder diffraction.

Bulk measurements show that below room temperature, a phase transition with a very broad hysteresis exists.⁵ Upon lowering the temperature, the electrical resistivity increases around 160 K and with increasing the temperature decreases around 290 K again.⁵ Both temperature dependencies are

identical below 160 K and above 290 K. A similar hysteresis is observed also in the temperature dependencies of the magnetic susceptibility, specific heat, and thermoelectric power. This transition was assigned to a crystallographic phase transformation, driven either by a valence transition or by charge-density wave type of ordering. Recent synchrotron x-ray diffraction experiments using small single crystals show that below room temperature broad superstructure peaks appear.⁷ The doubling of the CeCoAl-type structure is replaced by an ill-defined modulated structure. At least three different modulation periods are present, the dominant mode being close to a tripling of the basic CeCoAl cell. The (001) reflection, which is a very sensitive parameter regarding the superstructure modification, vanishes with lowering the temperature and at low temperatures attains not more than 3% of its high-temperature intensity. The intensity is shifted to a set of newly established reflections of the (00 l) type. While the c lattice parameter of the structure doubled with respect to the CeCoAl (called further as the $2c$ structure) shrinks across the phase transition by about 1%, the remaining two lattice parameters show much smaller variations. It was speculated that a charge ordering might be responsible for the structural change below room temperature.⁵

Very recently a detailed study of the structural determination accompanied by the thermal expansion, magnetization, and resistivity measurements on single crystals⁹ has been published. It is argued that the occurrence of polymorphism in CeRuSn resembles very strongly the situation in elemental cerium,¹⁰ where a Kondo effect¹¹ together with strong lattice vibrations¹² might be the driving force behind the structural transition. The other scenario is the one that deals with Ce entities in two different charge states leading to a charge separation.^{4,5,7}

Bulk measurement indicated two strongly hysteretic structural phase transitions to be present at 290 and 225 K on cooling. Based on x-ray diffraction, structure details have been determined for the relevant temperature ranges. At room temperature one observes the $2c$ structure and at low

temperatures a tripling of the c -axis parameter with respect to the CeCoAl type (we denote the later structure modification as the $3c$ structure) in agreement with suggestions based on the synchrotron experiment.⁷ At intermediate temperatures one observes a quintupling of the c -axis parameter with respect to the CeCoAl type (we denote this structure as the $5c$ structure) leading to five inequivalent positions for Ce, Ru, and Sn. This information prompted us to perform a neutron powder experiment with the aim to confirm these results and to determine the magnetic structure below $T_N = 2.7$ K. In this paper we summarize our experimental findings.

II. EXPERIMENT

Two batches of polycrystalline samples have been prepared by the arc melting of stoichiometric amounts of the constituent elements under a purified argon atmosphere at the Institut für Anorganische und Analytische Chemie, Universität Münster as described elsewhere.⁴ Several individual experiments have been performed at $E4$, $E6$, $E9$, and EXtreme Environment Diffractometer (EXED) instruments at Helmholtz-Zentrum Berlin and at the D1B instrument at Institute Laue Langevin, Grenoble. At $E4$, $E6$, and D1B we have used a neutron incident wavelength between 2.43 and 2.53 Å produced by (002) pyrolytic graphite (PG) monochromators with the aim to concentrate on the magnetic signal. At $E9$ a shorter wavelength of 1.79 Å led to a data set suitable for a detailed structural analysis. The time-of-flight (tof) instrument EXED gave us finally complementary information on both high-temperature and low-temperature structural details. Another diffraction experiment using this diffractometer, focused on the low-angle (large d spacing) region, revealed the existence of a complicated magnetic signal below T_N . In all cases, about 6 g of fine powder has been enclosed into a vanadium can together with a small amount of helium gas to improve the thermal contact. For the Rietveld-type data analysis we have used predominantly the computer code FULLPROF¹³ that is part of the WINPLOTR package.¹⁴

Magnetization and magnetic susceptibility measurements have been performed on a fine powder fixed by a small amount of a glue using a superconducting quantum interference device (SQUID) (Quantum Design) susceptometer between 1.8 and 350 K in fields up to 5.5 T. The diamagnetic glue and capsule contributions have been subtracted.

III. RESULTS

A. Magnetic susceptibility and magnetization

The temperature dependence of the inverse magnetic susceptibility measured with decreasing and increasing temperature on a fine fixed powder CeRuSn is shown in the upper inset of Fig. 1. It exhibits some small irregularities below ≈ 300 K implying that one cannot use a modified Curie-Weiss law in the whole temperature range. The irregularities are more pronounced for the warming-up curve. The difference between cooling and heating branches is most apparent between ≈ 150 and ≈ 310 K, i.e., in the same temperature range where, e.g., hysteretic behavior in thermal expansion is reported.⁹ The analysis that has to be restricted to reduced temperature intervals yields rather limited precision, but clearly suggests that the effective magnetic moment per Ce ion

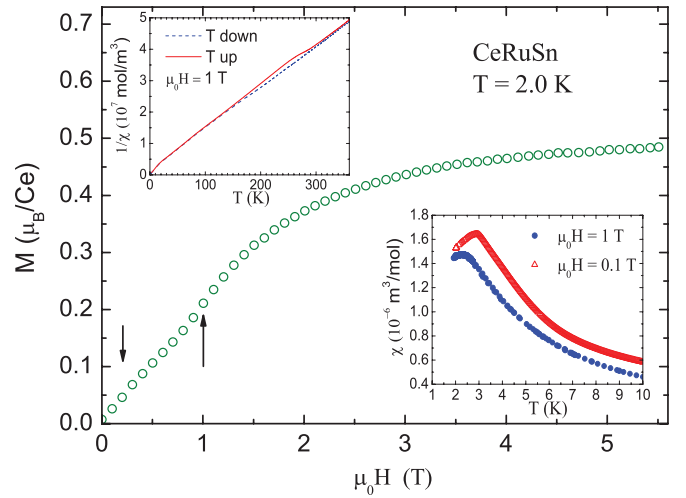


FIG. 1. (Color online) The field dependence of the magnetization measured on a fine fixed powder CeRuSn sample at 2.0 K in fields up to 5.5 T. The upper inset shows the temperature dependence of the inverse magnetic susceptibility measured in a field of 1 T with decreasing and increasing temperature in a large temperature range. The lower inset shows the low-temperature portion of the magnetic susceptibility measured in fields of 0.1 and 1 T.

is not compatible with the Ce^{3+} value. The fit to data above 300 K yields the effective moment of $2.10(3) \mu_B/\text{Ce}$, i.e., a larger value than has been reported,⁵ however, still lower than $2.54 \mu_B$, a value expected for the free Ce^{3+} . The paramagnetic Curie temperature amounts to $\theta_p = -1.9(4)$ K, suggesting the predominant AF exchange interactions in CeRuSn. As the temperature is lowered the effective moment decreases.

In the lower inset of Fig. 1 we show the low-temperature portion of the temperature dependence of the CeRuSn magnetic susceptibility measured in fields of 0.1 and 1 T. The maximum on the magnetic susceptibility that indicates the phase transition to the magnetically ordered state appears at 0.1 T at 2.8(1) K and shifts with increasingly applied fields to lower temperatures. In a field of 1 T it amounts to 2.2 K. This observation corroborates an AF order in CeRuSn. This conclusion is further supported by magnetization measurements. The magnetization curve obtained for CeRuSn at 2 K (i.e., below the proposed AF phase transition) is shown in the main panel of Fig. 1. After the initial fast increase, the Ce moment slowly saturates around a value of $0.49 \mu_B/\text{Ce}$ at a field of 5.5 T. The field derivative of the magnetization curve exhibits two maxima that are marked in Fig. 1 by arrows. These are interpreted either as a domain-repopulation effect or as a metamagnetic transition; the latter explanation being more probable for the upper field transition. Both findings are in good agreement with previous results⁵ that were obtained at 0.5 K except for the transition around 0.6 T found previously. Other magnetic measurement results are in good agreement with literature data.^{4,5,9}

B. Neutron diffraction

1. Crystal structure

In Fig. 2 we show the best fit to the data collected on the $E9$ diffractometer at 310 K, well above the hysteretic critical

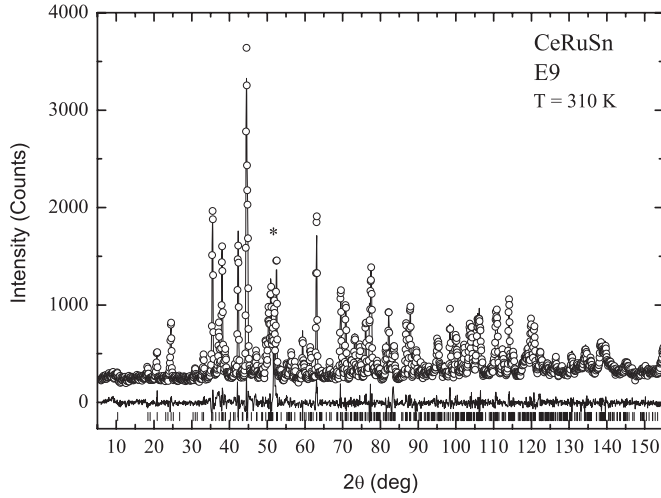


FIG. 2. The experimental (circles) diffraction pattern of CeRuSn powder taken at 310 K using E9 diffractometer together with the best fit (full line through points) to the crystal structure that is doubled along the c axis with respect to the CeCoAl-type structure (the $2c$ structure) and the difference between them (line at the bottom). Nuclear Bragg reflection positions are marked at the bottom. The strongest reflection due to an unidentified secondary phase is denoted by a star. For numerical results see Table I.

region obtained on a sample that has been previously exposed to elevated temperatures. The model used in the refinement is a simple doubling of the CeCoAl cell (the $2c$ structure) with two inequivalent Ce, Ru, and Sn atomic positions. In Table I we list numerical values resulting from the best fit to the $2c$ structural model. The results are in a very good agreement with the published data.⁴ However, we also observe an additional reflection that is not indexable within the $2c$ structural model and which is marked by a star in Fig. 2. As all attempts to account for this reflection failed we assume this reflection to be due to an unknown impurity. In Fig. 3 we show the temperature dependence of the integrated intensity of the (001) Bragg reflection as determined from an experiment using the D1B instrument.

The dependence clearly indicates that the reflection lowers its intensity significantly below 150 K, i.e., below the temperature that is reported to be below the crystal structure transformation temperature upon cooling.^{7,9} However, in contrary to the x-ray diffraction work that indicated 97% loss of (001) intensity we still observe $\approx 50\%$ of its high-temperature value. This suggests either that both techniques are sensitive to different sample volumes and/or that the powder sample behaves differently with respect to small single crystals used in x-ray experiments.^{7,9}

The low-temperature pattern taken at 5 K (i.e., above the AF transition temperature) with the EXED tof instrument in high-resolution mode cannot be reasonably fitted with the high-temperature $2c$ structure. The synchrotron work suggested the presence of a unit cell with the c -axis parameter three times larger with respect to the CeCoAl type of structure. Indeed, a small single crystal has been found to adopt such a crystal structure by the Prague group⁹ using x-ray scattering. However, it appears that the 5 K pattern cannot be satisfactorily fitted with such an enlarged unit cell and even not with the

TABLE I. Structural data for CeRuSn as determined from neutron diffraction data taken at the E9 diffractometer at 310 K.

CeRuSn	$T = 310$ K	Space group	$C2/m$
a (Å)	11.55270(10)		
b (Å)	4.74934(4)		
c (Å)	10.21304(10)		
β (deg)	102.975 (8)		
V (Å ³)	546.059 (8)		
Observed refl.	420		
R_B (%)	6.22		
R_F (%)	3.96		
χ^2	2.68		
Atomic positional parameters			
Label	Site	x	z
Ce1	$4i(x,0,z)$	0.1399(8)	0.4144(9)
Ce2	$4i(x,0,z)$	0.1250(7)	0.9072(7)
Ru1	$4i(x,0,z)$	0.1803(5)	0.6480(5)
Ru2	$4i(x,0,z)$	0.1984(5)	0.1951(5)
Sn1	$4i(x,0,z)$	0.4275(5)	0.3475(6)
Sn2	$4i(x,0,z)$	0.4009(5)	0.8487(6)
Label	B (Å ²)	Occupancy	
Ce1	0.64(29)	1.00(fixed)	
Ce2	0.41(24)	0.97(2)	
Ru1	0.45(19)	0.99(2)	
Ru2	0.96(19)	1.03(2)	
Sn1	0.68(19)	1.01(2)	
Sn2	0.80(21)	0.98(3)	

mixture of both, although the goodness of the fit (as judged by the χ^2) has improved by a factor of 3, at least. We have found that it can be explained only if one assumes the presence (in addition to the $2c$ and $3c$ superstructures) of yet other crystal modifications. At least $4c$ and $5c$ phases, which were identified during the synchrotron experiment,⁷ are found in our powder sample. Due to a large number of free parameters caused by

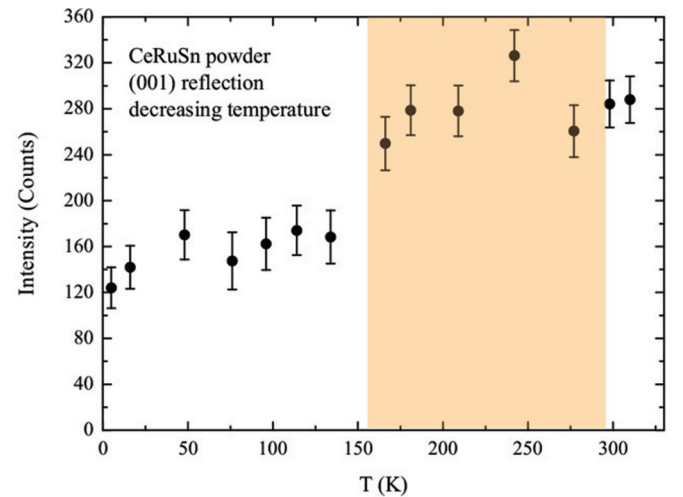


FIG. 3. (Color online) The temperature dependence of the (001) Bragg reflection as collected on the D1B diffractometer with decreasing temperature. The shaded area denotes the temperature region in which the structural transformation occurs.

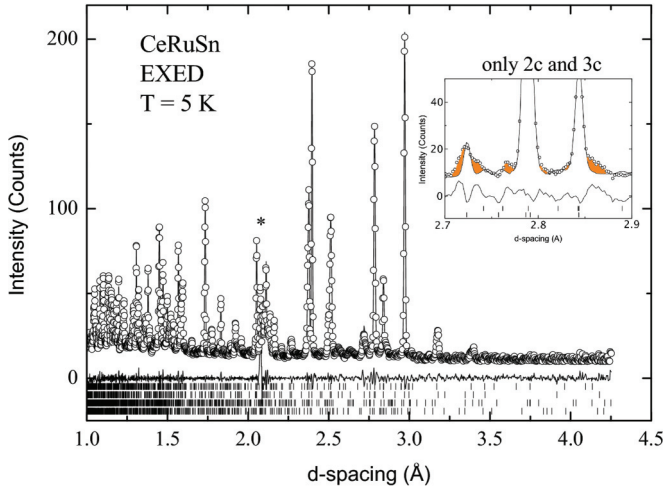


FIG. 4. (Color online) The experimental (circles) diffraction pattern of a CeRuSn powder taken at 5 K using EXED diffractometer together with the best fit (full line through points) assuming the presence of the 2c, 3c, 4c, and 5c structural modifications. While the former two were treated by the Rietveld refinement, the latter two were treated only by a profile matching fit. The difference between the experimental data and the calculated profile is represented by the line around zero. Bragg reflection positions due to 5c, 4c, 3c, and 2c nuclear structure modifications are marked by bars, starting from the bottom, respectively. The strongest reflection due to unidentified secondary phase is denoted by a star. For numerical results see Table II. In the inset we show a portion of the data together with the best fit assuming the presence of only the 2c and 3c structural modifications. The extra intensity that is not accounted for is denoted by (orange) shading.

positional degrees of freedom, the resulting fit parameters have limited precision. Instead of the complete Rietveld type of refinement we have treated the 4c and 5c phases by profile matching a Le Bail type of fit. In this way we find that the weight fraction ratio of the 2c and 3c phases within our sample is approximately 2 : 1 while 4c and 5c have only a few percents. The best fit to this type of model is shown in Fig. 4. In the inset we show the portion of the diffraction pattern with the best fit to data at 5 K omitting the 4c, 5c, and other phases. This fit shows that extra intensity is present in the vicinity of the 2c and 3c Bragg reflection positions (denoted in Fig. 4 inset by shading) proving that other structure modifications are present. However, as stated above, it is impossible to obtain realistic positional parameters of the 4c and 5c phases. In Table II we list the numerical values only for the 2c and 3c phases resulting from fit treating 4c and 5c phases by profile matching fit. The extra peak indicated in Fig. 4 with a star is the same as the extra peak found at room temperature in the E9 diffraction pattern (see Fig. 1). It cannot be indexed fully even by assuming the presence of higher-order phases. That is why we attribute this reflection to an unknown impurity. Lattice constant parameters as listed in Table II are systematically larger than those listed in Table I derived from the E9 data at 310 K. This is an experimental effect due to the uncertainties in the time-of-flight experiment.

The apparent coexistence of different structures raises immediately a question regarding the phase purity also at

TABLE II. Structural data for the 2c and 3c structural models of CeRuSn as determined from neutron diffraction. Data are determined from Rietveld-type fit to 2c and 3c phases together with profile matching fit to 4c and 5c phases to data taken at EXED at 5 K.

CeRuSn	$T = 5$ K	Space group	$C2/m$
Phase	2c	3c	
a (Å)	11.66448(3)	11.67737(3)	
b (Å)	4.79291(2)	4.79291(1)	
c (Å)	10.31064(3)	15.41933(3)	
β (deg)	103.115(3)	103.369(5)	
V (Å ³)	561.399(3)	839.609(3)	
Observed refl.	542	804	
R_B (%)	3.68	4.39	
R_F (%)	5.28	8.58	
χ^2	2.93		
Phase 2c	Atomic positional parameters		
Label	Site	x	z
Ce1	$4i(x,0,z)$	0.1327(14)	0.4114(9)
Ce2	$4i(x,0,z)$	0.1292(13)	0.9044(10)
Ru1	$4i(x,0,z)$	0.1852(8)	0.6457(7)
Ru2	$4i(x,0,z)$	0.1909(9)	0.1953(6)
Sn1	$4i(x,0,z)$	0.4176(12)	0.3482(8)
Sn2	$4i(x,0,z)$	0.4137(12)	0.8494(8)
Phase 3c	Atomic positional parameters		
Label	Site	x	z
Ce1	$4i(x,0,z)$	0.128(5)	0.105(3)
Ce2	$4i(x,0,z)$	0.134(5)	0.443(3)
Ce3	$4i(x,0,z)$	0.125(5)	0.775(3)
Ru1	$4i(x,0,z)$	0.196(4)	0.277(2)
Ru2	$4i(x,0,z)$	0.205(3)	0.634(1)
Ru3	$4i(x,0,z)$	0.195(4)	0.946(2)
Sn1	$4i(x,0,z)$	0.410(5)	0.064(3)
Sn2	$4i(x,0,z)$	0.414(4)	0.396(2)
Sn3	$4i(x,0,z)$	0.426(4)	0.739(2)

elevated temperatures. It appears that the fit of the data taken at 310 K immediately after the low-temperature experiments leads to about 15 vol.% of the 3c phase. It seems that a 100% 2c phase purity cannot be achieved even by exposing the sample to temperatures as high as 520 K. This is documented by the temperature dependence of the 2c phase fraction together with lattice parameters shown in Fig. 5 as obtained on the E6 diffractometer. Comparing the fits obtained at 300 K before and after cooling the sample down to 2 K, a larger 3c phase fraction is found for the latter situation. The amount of the 3c phase is further reduced after heat treatment at 520 K. However, even at this temperature one detects traces of the 3c phase present in the sample.

Starting from a sample that has not been thermally treated, the c -axis parameter of the 2c phase decreases with decreasing the temperature. At 2 K its value reduces by $\approx 0.7\%$ with respect to its room-temperature value. This reduction is somewhat smaller than the reduction found in the synchrotron experiment,⁷ but the overall behavior remains comparable. While the a and b lattice parameters of the 2c phase show rather small hysteresis around 200 K between cooling and warming the c -axis parameter shows significant difference around this

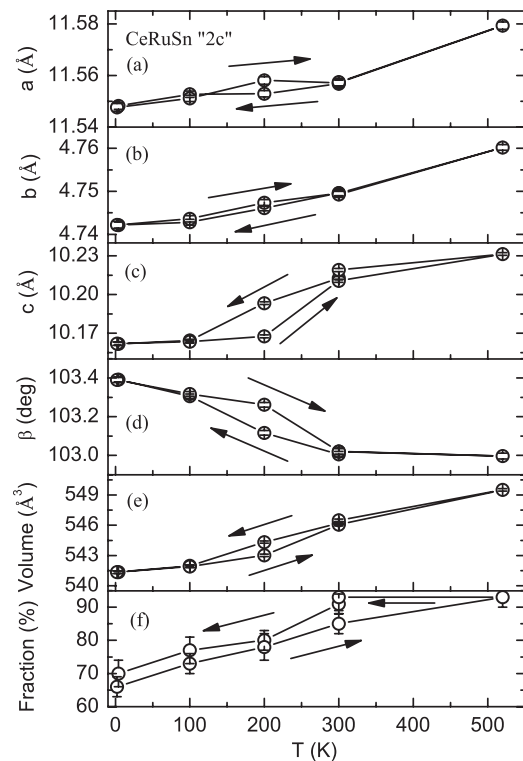


FIG. 5. (a–d) Temperature dependence of the “2c” structural phase of CeRuSn principal lattice parameters determined from the best fits to neutron data taken at the $E6$ diffractometer. The volume of this phase is shown in panel (e) and the approximate weight percentage of the “2c” phase is shown in panel (f).

temperature, in agreement with the synchrotron study.⁷ The monoclinic angle β shows similar remarkable hysteresis on the cooling and warming branches. This hysteresis matches with the proposed 5c phase existence temperature range⁹ and the hysteretic range seen on the magnetic susceptibility.

2. Antiferromagnetic structure

In Fig. 6 we present a contour graph showing the development of diffracted intensities of the CeRuSn powder sample in the vicinity of the (001) reflection at low temperatures as measured on the $E4$ diffractometer. The two weak Bragg reflections appearing below $\approx 2.8(1)$ K (denoted by the black dashed line) are interpreted as being of magnetic origin. Their onset agrees well with the T_N inferred from magnetic bulk measurements. We could index them with a general propagation vector $\mathbf{q}_1 = (0, 0, \approx 0.30)$ with respect to the 2c phase and labeled them at the top of Fig. 6 accordingly. However, the precise determination of the propagation vector is ambiguous. The temperature dependence of their integrated intensities is shown in Fig. 7. While the $(001)^-$ reflection gradually saturates when approaching the lowest temperature, the $(100)^-$ steadily increases upon cooling. It should be noted that below T_N no increase of intensity is seen on top of the (001) reflection. The appearance of the two magnetic reflections seen with the $E4$ instrument is corroborated by the appearance of yet other magnetic reflections in patterns taken at 1.8 K using D1B and $E6$ instruments. These data are shown together with data taken above the T_N and their difference in

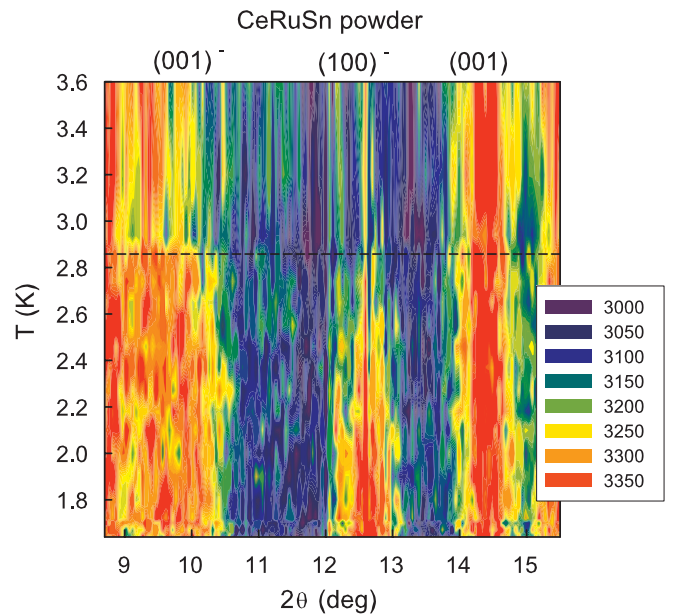


FIG. 6. (Color online) The contour graph showing the development of diffracted intensities of CeRuSn powder sample in the vicinity of the (001) reflection at low temperatures. The two weak (but strongest) magnetic Bragg reflections appearing below approximately $T_N = 2.8(1)$ K (black dashed line) are labeled at the top. Neutron counts are color coded according to the scale given on the right.

Figs. 8(a) and 8(b), respectively. The $E6$ and D1B instruments are complementary to each other. While $E6$ was used in a mode that maximizes the intensity on account of the resolution, D1B has better resolution at lower diffraction angles. Reflections due to magnetic order seen at both instruments can be indexed by a similar, but not exactly the same propagation vector.

There are two facts worth noting. The first one is that magnetic reflections appear to be broader than the nuclear ones and second that there might be still very weak magnetic

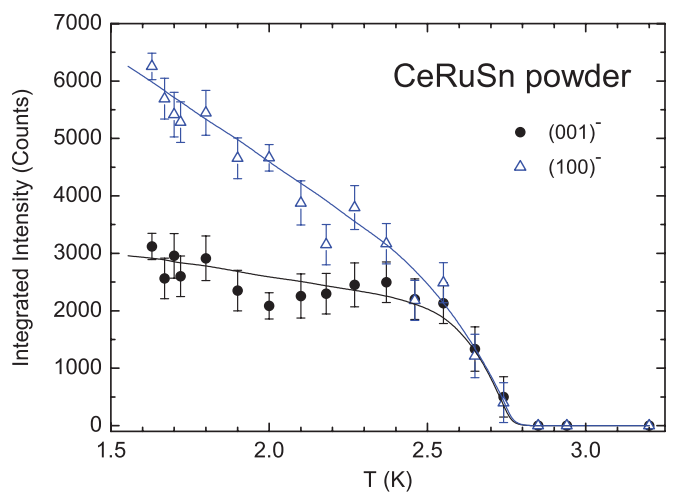


FIG. 7. (Color online) The temperature dependence of the integrated intensities of the two magnetic reflections labeled in Fig. 6 as $(001)^-$ and $(100)^-$. The magnetic phase transition identified from the current measurement is $T_N = 2.8(1)$ K. Full lines are guides for the eye.

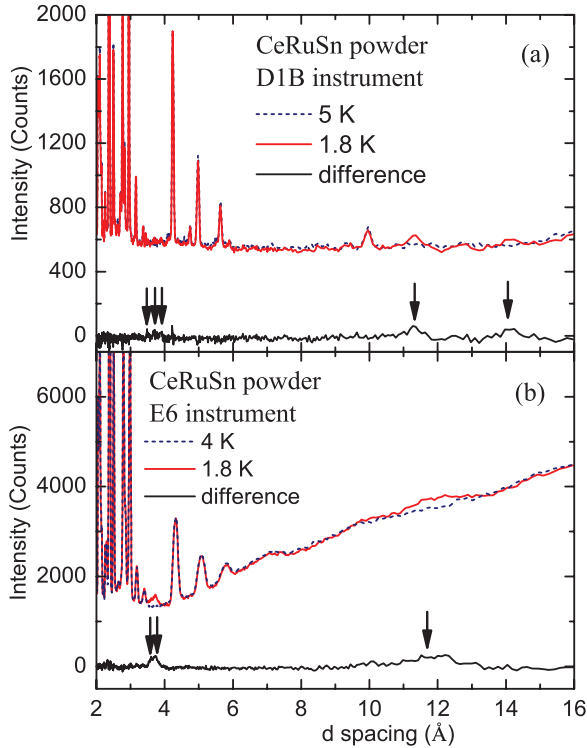


FIG. 8. (Color online) Experimental neutron diffraction profiles obtained on a powder CeRuSn sample at low temperatures using the (a) D1B and (b) E6 diffractometers as a function of the d spacing. For each diffractometer, we show a diffractogram taken above the magnetic phase transition, at the lowest temperature of 1.8 K and the difference between them. Reflections that appear below T_N due to AF order are shown for both panels by arrows.

reflections present in the D1B pattern that can be accounted for by another propagation vector $\mathbf{q}_2 = (0, 0, \approx 0.43)$.

The determination of the AF structure turned out to be rather difficult due to small intensities of magnetic reflections and due to multiphase nature of the powder sample. This prompted us to perform yet another diffraction experiment using the EXED diffractometer in the high intensity mode, this time focused on the large d -spacing reflections, i.e., optimizing the instrument to have maximum flux for reflections having large d spacing that appear at low diffraction angles. These data, taken above T_N at 5 K and below T_N at 1.8 K, are shown in Fig. 9, together with their difference. As it can be seen, the data above T_N show the presence of several Bragg reflections around the d spacing of 10 Å. If the sample would contain solely the $2c$ structure, then only the (001) reflection is expected, thereby pointing to the presence of other structural phases. At least four structural phases denoted as $2c$, $3c$, $4c$, and $5c$ are necessary to account for all the observed reflections at 5 K. And even then, one has to assume lifting of the extinction rules connected with the $C2/m$ space group. The vertical marks shown in the inset of Fig. 9 are structural Bragg positions calculated by assuming the absence of any extinction rules (in contrast to crosses that do preserve them). Only in this way one can index all the structural Bragg reflections seen at 5 K. It is, however, clear that with such a set of free parameters it is not possible to perform a Rietveld type of refinement. In the inset of Fig. 9 we therefore show merely

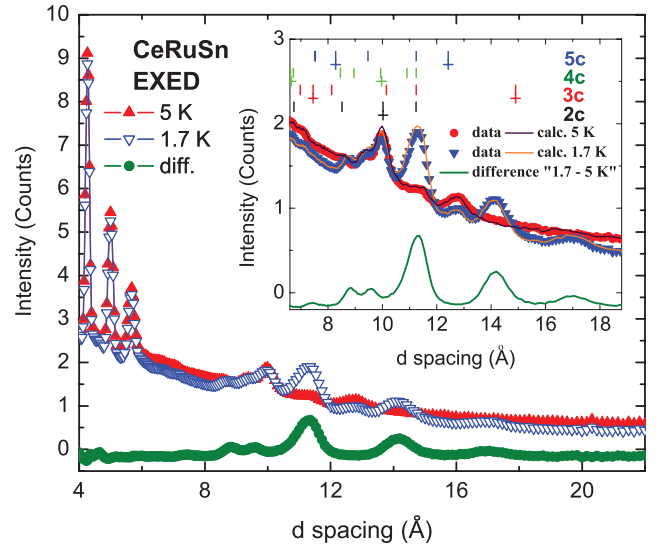


FIG. 9. (Color online) Experimental neutron diffraction profiles obtained on a powder CeRuSn sample at low temperatures using the time-of-flight diffractometer EXED as a function of the d spacing. Data taken above the magnetic phase transition temperature T_N can be fully indexed only assuming the presence of at least four structural phases denoted as $2c$, $3c$, $4c$, and $5c$ (the positions of the Bragg reflections that preserves $C2/m$ space group extinction rules are cross-marked in the inset) that have lost the C -type glide plane (shown as vertical ticks). At 1.7 K, new Bragg reflections appear. The difference between the two temperatures is shown in green full circles in the main panel and by a solid line in the inset. In the same inset we show also the calculated profile generated on the basis of the best fit to the pattern taken on the D1B instrument (see main text).

the profile-matching type of fit assuming the presence of $2c$, $3c$, $4c$, and $5c$ phases.

As the temperature is decreased below the magnetic phase transition temperature, a set of new Bragg reflections appears (see the difference lines in Figs. 8 and 9). Having a multiphase system, attempts to index magnetic Bragg reflections is ambiguous as it is not clear to which paramagnetic phase these magnetic reflections belong. In the case of CeRuSn the situation is even more complicated as the phases present in the sample differ only by the c -axis parameters that are related by a simple multiplication. This is why we will assume in the following text that all magnetic reflections are associated merely with the $2c$ phase. Then, all magnetic reflections can be indexed by two propagation vectors as identified above in the E4 and D1B experiments, namely $\mathbf{q}_1 = (0, 0, \approx 0.30)$ and $\mathbf{q}_2 = (0, 0, \approx 0.43)$.

To generate all possible magnetic moment configurations that are in accordance with this space group and propagation vectors, we have used the group symmetry analysis as developed by Bertaut.¹⁵ Let us assume for a moment an undistorted $2c$ phase with the $C2/m$ space group. All the magnetic Ce atoms are situated at the $4i$ Wyckoff position with the local symmetry m . This suggests that Ce magnetic moments can be oriented either parallel or perpendicular to the b axis. For each Ce1 and Ce2 site, there are two pairs of Ce moments that are related by the glide plane symmetry that relates the direction and moment magnitude within these

pairs. However, it became clear that in this case one cannot generate any intensity on magnetic reflection appearing around 11.5 Å (see Figs. 8 and 9) and thus lowering the symmetry is necessary. This is in agreement with the nuclear structure data shown in Fig. 9 which evidence a distortion to explain all the observed high d -spacing reflections. This in turn, however, means that fits assuming the undistorted $C2/m$ space group are not correct. However, meaningful fits using the lower symmetry models are impossible due to a low intensity of the “extra” reflections. Our data are insensitive to the distortion and a large number of heavily overlapping Bragg reflections together with a large number of structural fit parameters make the situation even more difficult. One has to bear in mind that data given in Table II are neglecting this subtle distortion.

Within the distorted structure the magnetic moments are, according to the symmetry analysis, allowed to have any orientation. There is also no symmetry relation between them, a phase shift introduced by propagation vectors being the only constraint. The simplest magnetic moment configuration we can think of is a sine-wave-modulated magnetic structure propagating along the c axis. However, different Cartesian components can be modulated with one or both propagation vectors leading thus to more complicated magnetic structures that include even distorted cycloidal and spiral ones. After an extensive trial and error approach we came to the conclusion that the b -axis component is negligible in all fits that agree relatively well with the low-temperature data.

The best agreement between the data and the fit is indeed achieved by a complicated distorted cycloidal magnetic structure shown in Fig. 10. In fact, it is very close to a collinear sine-wave-modulated structure. However, the deviation from the collinearity is important as some of the observed reflections that are observed would be negligibly small. The best fit to our data at 1.7 K is shown in Fig. 11. The same set of refined structural and magnetic parameters describes also other sets of experimental data taken using other instruments (*E6* and *EXED*). This is documented for instance in Fig. 9 by calculated profiles shown by full lines through the experimental data above and below the magnetic phase transition temperature. These are calculated on the basis of the best fit to the D1B

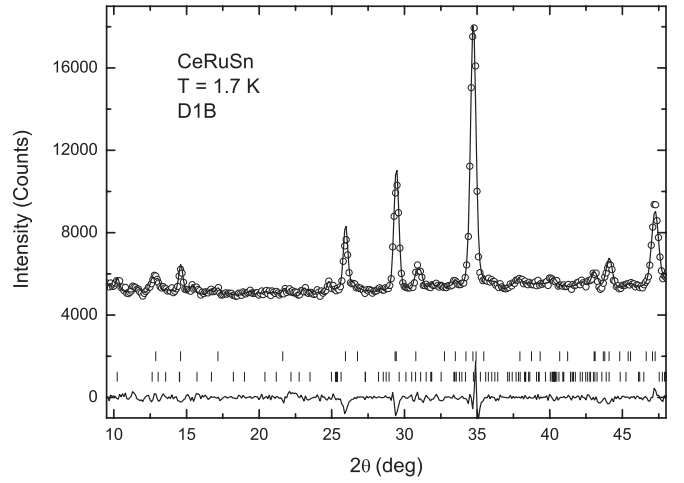


FIG. 11. Portion of the experimental neutron diffraction profile obtained on a powder CeRuSn sample at low temperatures using the D1B diffractometer. Data taken at 1.7 K are shown by open points, the best fit by a full line through these points and the difference between experimental data and the fit by a full line at the bottom. Positions of the magnetic reflections are marked at the bottom by vertical bars. The second row from the bottom denotes positions of nuclear reflections belonging to the $2c$ phase. For clarity reasons, all reflections originating from the $3c$ and $4c$ and from $\lambda/2$ contamination are omitted.

data, taking into account only the specific parameters (e.g., resolution) of the relevant diffractometers and keeping all other parameters fixed. The agreement is not perfect but satisfactory, giving us a confidence concerning the correctness of the determined magnetic structure.

Having a rather satisfactory solution, we have also tried to ease the relation between the moment magnitude between the two Ce sites. It appears that our data are insensitive to such a degree of freedom. The fit is not improved and the difference between the moment situated at the site with short Ce–Ru bond (Ce1 site) is only marginally smaller than that one on the Ce site with a larger Ce–Ru bond (Ce2 site). The results of this type of fit are summarized in Table III. As it can be seen both moments attain $\approx 0.7 \mu_B$.

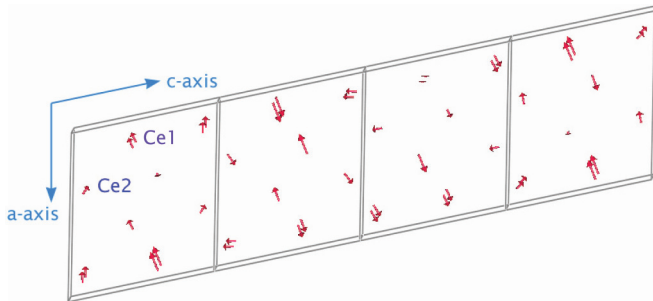


FIG. 10. (Color online) Schematic representation of the magnetic structure of CeRuSn at low temperatures. On the figure the $a \times b \times 4c$ chemical unit cell with only Ce magnetic moments is shown to document the propagation along the c axis. The two Ce sites with different geometrical surrounding are indicated: The Ce1 has two Ru neighbors at a distance that is much smaller than the distance between the Ce2 site and its two Ru neighbors.

TABLE III. Magnetic structure parameters of powder CeRuSn sample determined from Rietveld-type fit assuming that only (independent) Ce magnetic moments of the $2c$ phase orders magnetically below $T_N = 2.8(1)$ K with both of the two propagation vectors.

CeRuSn	$T = 1.8$ K		D1B
	$\mu_x (\mu_B)$	$\mu_y (\mu_B)$	$\mu_z (\mu_B)$
Ce1	0.75(16)	0	0.14(9)
Ce2	0.68(13)	0	0.36(11)
Propagation vectors			
q_1	[0 0 0.297(8)]		
q_2	[0 0 0.438(10)]		
Observed refl.	171		
R_p (%)	4.75		
R_M (%)	11.3		

IV. DISCUSSION AND CONCLUSION

There is no doubt that CeRuSn exhibits a quite unique behavior upon cooling. The (001) reflection intensity reduces upon decreasing the temperature by about 50% although other reflections show hardly any intensity variation. This points to changes in the structure factor determining the (001) reflection. It appears that the magnitude of this reflection is critically dependent on the positional deviations of atoms from the higher symmetry positions of the undistorted CeCoAl structure type. In other words, it seems that upon cooling, Ce1 and Ce2 sites become more equivalent. There is, however, another scenario possible. Namely, that parts of the sample undergoes another structural transition and that simply the volume of the $2c$ phase decreases. Our data support this second scenario. The appearance of reflections indexable with $3c$ and higher multiplets along the c axis suggest that we deal here with a multiphase system.

The already complicated crystal structure that is derived from the original monoclinic structure of the CeCoAl type by the splitting of the crystallographic sites, which consequently leads to a doubling of the c -axis parameter, becomes just below room temperature even more complicated. A question that remains is what is the driving force for the structural phase transition. A possibility is a creation of a Verwey-type structural distortion^{16,17} driven by a charge order. The presence of a charge order and associated lattice modification (with respect to the CeCoAl-type structure) has been suggested to be present in the case of CeRuSn already at high temperatures. Indeed, short and long Ce–Ru bondings lead to two different Ce valence states as documented by structural and physical property data. A further splitting of the Ce, Ru, and Sn sites leads to phases that are elongated in the c -axis direction. At this point we argue that this is a consequence of another type of charge order that should be reflected in fractions of $\text{Ce}^{(4-\delta)+}$ and trivalent Ce^{3+} states and different bond lengths. The complexity and a large number of free parameters prevent, however, the determination of the structural details of the $4c$ and higher phases. The thermal cycling also suggests that the critical region where the additional structural transformation occurs is highly hysteretic as it is related to the amount of different phases found at 300 K before and after cooling the system to low temperatures or heating up to 520 K. The difference in phase volume fraction is in a range of several percents. At this point we argue that the changes of the c lattice parameter of the $2c$ phase are responsible for significant stress within the grains and multiphase character of the sample and the observed history dependencies. This, in turn, could also be the reason for the different behavior of the powder sample and the small single crystal studied previously by synchrotron radiation.⁷

The single-crystal behavior has been explained by a presence of ill-defined ground state where several phases compete. This finding is common to both studies. What is different is the amount of these phases [as related to the reduction of the (001) reflection] found in the single crystal, where the (001) reflection preserves only about 3% of its room-temperature intensity and the powder sample where the intensity decreases by a factor of 2. Let us note that the difference in the (001) behavior between the x-ray and neutron experiments cannot be explained by the different scattering

factors of individual elements sensed by the two techniques. A possibility would be that samples with a slightly different stoichiometry have been used. It is well known that a tiny variation in stoichiometry can stabilize both the magnetic and crystal structures having different propagation vectors. However, we have here a stoichiometric compound prepared several times by different groups. The overall behavior and results are reproducible and comparable between groups although details can vary somewhat even between subsequent cycling on the same sample. This suggests that rather than the stoichiometry of the sample its physical state plays a role.

The crystal structure of CeRuSn is derived from that of CeCoAl by a doubling of the c -axis parameter. This is caused by tiny shifts of Ce/Ru/Sn atoms from their original positions resulting in two inequivalent positions. A phase transformation of this kind does not require any change in stoichiometry and other, more exotic causes are possible, e.g., a valence change of the Ce. Therefore, it seems unlikely that stoichiometric issues are the driving force. Of course, this does not mean that Sn off-stoichiometry may not be present. Such might be responsible for different amount of individual phases in different samples at particular conditions.

There is no doubt about the AF ordering of CeRuSn at low temperatures. It appears however, that the details remain elusive. The reason is a large number of fit parameters connected with a multiphase character of the powder sample together with a further reduction of the symmetry and existence of two propagation vectors. Assuming only the $2c$ crystal structure modification present in the sample there are two propagation vectors necessary to describe the presence of all magnetic reflections. Symmetry analysis allows for all magnetic moment directions. Nevertheless, the best solution that gives a reasonable agreement with the observed data is found for a cycloidal magnetic structure with Ce moments confined to the ac plane. The a - and c -axis components are nearly equal for all sites and our data are not sensitive to further details. It is interesting to note that we have anticipated a different magnetic moment at the Ce1 and Ce2 sites that would reflect different Ce valence states due to strikingly different Ce–Ru bonds. On the contrary, we do not obtain significantly different Ce magnetic moment magnitudes at the two crystallographic sites. They are, with a value of $\approx 0.7 \mu_B$, strongly reduced with respect to the free ion Ce^{3+} value of $2.14 \mu_B$. This suggests that Kondo screening plays a significant role in the physics of CeRuSn. It is clear that further studies are needed, perhaps using a fresh single crystal, to exclude, for instance, the possibility that one propagation vector is associated with one structural phase and the second one with another phase. One needs to determine the details of the AF structure that were not possible to be determined in this work. In particular, we hope that single-crystal work can shed some more light on phases between individual moments and it might be more sensitive to questions whether the moments on the two different sites propagate with the same or different propagation vector and what magnitude they have. All these parameters may change to a certain degree with respect to results obtained here. The reasons could be either due to the different behavior of the single crystalline samples and/or due to the new type of information available from single-crystal work that is not possible to be obtained from powder neutron diffraction.

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