Crystal Chemistry and Physics of UCd$_{11}$

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ABSTRACT: In the phase diagram U-Cd, only one compound has been identified so far—UCd$_{11}$ (space group Pm3m). Since the discovery of this material, the physical properties of UCd$_{11}$ have attracted a considerable amount of attention. In particular, its complex magnetic phase diagram—as a result of tuning with magnetic field or pressure—is not well-understood. From a chemical perspective, a range of lattice parameter values have been reported, suggesting a possibility of a considerable homogeneity range, i.e., UCd$_{11-x}$. In this work, we perform a simultaneous study of crystallographic features coupled with measurements of physical properties. This work sheds light on the delicate relationship between the intrinsic crystal chemistry and magnetic properties of UCd$_{11}$.

1. INTRODUCTION

The initial interest in the compounds of cadmium and uranium was motivated by the possible application of these materials in reprocessing of nuclear fuels. Within the uranium–cadmium system, only one compound has been reported so far—denoted as UCd$_{11}$ (structure type BaCd$_{11}$). Its detailed structure determination using neutron diffraction revealed strong cadmium deficiency, distributed more or less equally over all occupied Cd sites. As a result, the cadmium-deficient composition of UCd$_{2.5}$ was reported. Measurements of magnetic properties of UCd$_{11}$ revealed that this compound orders antiferromagnetically below $T_N = 5$ K. However, what has really spiked scientific interest in this material was an enhancement of the effective electron mass, as evidenced by one of the largest electronic specific heat coefficients among known uranium-based materials. Similarly, several metamagnetic transitions have also been observed. The nature of all of these transitions remains unclear. Overall, while $\mu$SR spectroscopy and neutron diffraction experiments on UCd$_{11}$ confirmed bulk magnetic ordering below $T_N$, the properties of this material appear to be rather intricate and remain to be understood completely.

Atomic arrangement in UCd$_{11}$, assuming complete occupancy of all Cd sites, is fairly complex, hosting uranium-centered polyhedra coordinated by 20 cadmium atoms, see Figure 1. Four cadmium sites and one uranium site exist in UCd$_{11}$. It is likely that the origin of peculiar magnetism in UCd$_{11}$ stems from its complex crystal structure (Figures 2). A large span of lattice parameter values is reported in the literature (9.248 Å $\leq a \leq 9.29$ Å), suggesting a possible homogeneity range as a result of partial occupancy on the cadmium sites. Additionally, a variation of electronic specific heat coefficient $\gamma$ from 803 to 950 mJ mol$^{-1}$ K$^{-2}$ has been observed. Similar to other uranium-based systems, a delicate interplay between intrinsic crystal chemistry and physical properties can only be revealed by a comprehensive analysis on both macro- and microscales.
2. METHODS

2.1. Synthesis. Six U-Cd samples with three U:Cd ratios (6.3:93.7, 8.3:91.7, and 10.3:89.7, see Table S1) were prepared by direct reaction of the components. All sample preparation and handling were performed in the specialized laboratory equipped with an argon-filled glovebox system (MBraun, H2O/O2 < 0.1 ppm).

Similar to previous studies, single crystals of UCd11 were obtained by melting (i) stoichiometric and (ii) slightly off-stoichiometric amounts of uranium (powder prepared from sheet, Goodfellow, 99.98%) and cadmium (pieces, Alfa Aesar, >99.9%). The tantalum tubes with the starting mixture of the elements were sealed under an argon atmosphere, heated to 420 °C, and then slowly cooled back to room temperature at a rate of 2.5 °C per hour. The resultant product was a gray, polycrystalline powder with some μm-sized crystals.

2.2. Materials Characterization. Powder X-ray diffraction was performed on a Huber G670 imaging-plate Guinier camera with a Ge-monochromator (CuKα, λ = 1.54056 Å). LaB6 was used as a standard. Phase identification was done using WinXPow software. For all samples, in addition to the main UCd11 phase which is homogeneous (Figure 3), a small amount of either elemental Cd (samples 1–5) or elemental U (sample 6) is seen in the powder X-ray diffraction data (see Figure 4 and Table S2). While it is not possible to estimate the exact amount of Cd or U admixture, the relative amounts (compared to other samples in the study) were found from the ratio of the intensities of the strongest UCd11 (2θ = 31.9 degrees) to the strongest Cd (2θ = 38.3 degrees) peaks. The lattice parameters were determined by a least-squares refinement using the peak positions extracted by profile fitting (WinCSD software38, Figure 5).

Small crystals on the order of ca. 30 μm were suitable for single-crystal diffraction experiments. The diffraction data were collected using a Rigaku AFC7 diffractometer equipped with a Saturn 724+ CCD detector and a MoKα radiation source (λ = 0.71073 Å). The WinCSD38 software packages were used for data analysis. The results of the crystallographic characterization of UCd11 are provided in Tables 1–3 and S2. From the structural refinement, no variation in stoichiometry or occupancy was observed between various UCd11 samples. Thus, all samples’ stoichiometry is UCd11 within experimental error bars.

For metallographic investigations, pieces of UCd11 samples were embedded into a polymer matrix using a hot mounting press (ProntoPress 10). SiC paper and diamond powder with grain sizes of 3 μm or smaller were used for surface polishing. Chemical composition was studied on polished samples using energy-dispersive X-ray spectroscopy with a Jeol JSM 6610 scanning electron microscope equipped with an UltraDry EDS detector (Thermo Fisher NSS7). The semiquantitative analysis was performed with 25 keV acceleration voltage and ≈3 nA beam current. The resultant backscatter electron micrograph is shown in Figure 3. Aside from cavities (black), no inclusions of secondary phases have been detected. Elemental mapping of Cd (panel (b)) and U (panel (c)) indicates that the uranium content remains constant within the sample (8.5 at. % of U).

2.3. Physical Property Measurements. The analysis of magnetism in UCd11 was performed on polycrystalline samples. For
most of the samples, either elemental U or Cd was present in addition to the UCd\textsubscript{11} phase (see Figure 4). The magnetic properties were studied using a Quantum Design (QD) Magnetic Property Measurement System for the temperature range from \(T = 1.8\) K to \(T = 300\) K and for applied magnetic fields up to \(H = 7\) T. The specific heat data were collected on a Quantum Design Physical Property Measurement System in the temperature range from \(T = 0.4\) K to \(T = 10\) K for magnetic fields up to \(H = 9\) T. Due to the polycrystalline powder-like nature of the samples, it was not possible to carry out electrical resistivity measurements.

3. RESULTS AND DISCUSSION

The UCd\textsubscript{11} compound crystallizes in the cubic BaHg\textsubscript{11} structure type and decomposes peritectically at \(T = 473\) °C.\textsuperscript{1} It was previously shown that the structure of UCd\textsubscript{11} is rather robust against application of pressure—the unit cell can be compressed by nearly 20\% (for \(p = 20\) GPa) without any discernible structural phase transitions.\textsuperscript{26} While some structural information has been reported previously, the possibility of a homogeneity range in UCd\textsubscript{11} has not been investigated.\textsuperscript{1,10,11,9−14,23}

In the current study, high-quality single-crystal data was obtained for crystals extracted from samples 4 and 5. The collection of diffraction intensities was made on an irregular single crystalline specimen with dimensions of \(12 \times 12 \times 30\) μm\textsuperscript{3}. Crystallographic information for the single-crystal UCd\textsubscript{11} (sample 4), together with further details of the single-crystal X-ray diffraction experiment, are presented in Tables 1 and 2. The collected diffraction data were indexed using the cubic lattice with the lattice parameter of 9.2970(3) Å, being close to the upper limit of those reported earlier (9.248 Å \(\leq a \leq 9.29\) Å).\textsuperscript{1,10,11,9−14,23} The extinction conditions in the measured data set agreed well with the primitive lattice of the BaHg\textsubscript{11} structure type indicated in ref 9. Application of the charge-flipping technique allowed to establish the basic atomic arrangement formed by one uranium and four cadmium positions (Figure 1, top). It is important to note that the displacement parameter for the Cd2 position was strikingly large in comparison with three other cadmium sites. Refinement of this structure model using anisotropic approximation of atomic displacement revealed strong anisotropy of the atomic displacement for the Cd2 site. Calculation of the residual electronic density with isotropic displacement for this position indicates nondescribed density on both sides of the position along the space diagonal of the unit cell (Figure 1, middle), making a split necessary (Figure 1, bottom). The final refinement resulted in \(R_F\) of 0.033 for 579 reflections used. The attempts to resolve this split by lowering

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**Figure 3.** Backscatter electron micrograph of a polished UCd\textsubscript{11} sample (sample 5). Panels (b) and (c) show elemental mappings for the same region, with Cd (pink) and U (green), respectively. No distinguishable variation in the sample composition has been observed.

**Figure 4.** Powder X-ray diffraction data for the UCd\textsubscript{11} samples used in the current study. Black vertical symbols mark the positions of the reflections corresponding to the UCd\textsubscript{11} phase, while red symbols correspond to LaB\textsubscript{6} used as a standard. The gray and yellow regions mark the peak positions of elemental Cd and elemental U, respectively. For these, only the peaks which do not overlap with either UCd\textsubscript{11} or LaB\textsubscript{6} are shown.
the symmetry within the same Laue class failed: despite the larger number of refined parameters, the residual values were not reduced (0.039 in the space group $P4_3m$ and 0.052 in $P2_3$), and the strong anisotropy of the Cd2 position remained unchanged. An attempt to implement the defect (approximately 14%, as suggested in ref 9) on all Cd positions led to a significant increase of $R_{\text{F}}$ to 0.056. Final atomic coordinates, displacement parameters, and interatomic distances are listed in Tables 2, 3, and S2, respectively.

The crystal structures of the BaH$_{11}$ structure type are usually described as a packing of the large cation-centered polyhedrons (UCd$_{20}$ in the case of UCd$_{11}$) with 20 vertices located at (0 1/2 1/2) and Cd-centered cuboctahedrons (CdCd$_{13}$) at (0 0 0)—see, for example, Figure 2 (top panel) in refs 39 and 40. This description does not allow us to understand the reasons for the split of the Cd2 site. Besides filled cages in the Cd framework, two types of smaller empty voids exist: in the nonsplit model, a cubic one is located at (1/2 1/2 1/2) and the four-capped trigonal prismatic one at (1/2 0 0) (see Figure 2, bottom panel); in the split model, both are distorted. As it was recently shown for several structures,
empty cubic voids in the frameworks are not stable and undergo deformation either toward tetragonal antiprisms or toward tetrahedron stars like in Ce₃Ga₄₄Pt,¹¹ R₃Ga₄T,¹² Ce₃PdGa₁₂,¹³ and PuGa.¹⁴ The split of Cd2 position in UCd₁ can be understood as a result of the structural transformation according to the latter scenario. Similar strong displacement anisotropy was observed in the ternary derivative YbPdGa, but not in the prototype BaHg₁₁P₁₂.²⁰

The strong displacement anisotropy of the Cd2 position may have two origins: the dynamic and the static one. Independently of the origin, the Cd2 position or its split positions is 3.8 Å apart from the U one. Thus, this should not significantly influence the electronic state of U and, therefore, its magnetic moment. On the other hand, if the Cd positions located in the first coordination sphere of U are not fully occupied, as proposed by ref 9, the magnetic properties of uranium may change. The comparison of the magnetic susceptibility measurements of current and previous works reveals the same ordering temperature and effective magnetic moment (see below), which indicates that the electronic state of uranium is in fact the same across all UCd₁ samples reported so far.

Partial occupancy on the Cd sites has been previously suggested, resulting in UCd₁₅ composition.¹⁴ It is important to note that the analysis of the crystal structure of UCd₁₁ in ref 9 was carried out using neutron powder diffraction experiments. The sample investigated in ref 9 shows the lattice parameter on the lower end of the spectrum of known values (Figure 5a). It was not possible to reproduce this value of the lattice parameter in the current study—the single-crystal investigations yielded larger lattice parameter values. It is possible, however, that the defects on Cd sites reported in ref 9 may appear due to the thermal treatment during the single-crystal growth.

Magnetic properties of UCd₁₁ have been previously studied using a number of experimental techniques.¹⁰−¹² The entrance into antiferromagnetic state is marked by a characteristic anomaly around Tₛ = 5 K. For all samples from the current study, a cusp-like feature has been observed in temperature-dependent magnetization data at T = 5.1 ± 0.1 K, as evidenced by the derivative dM/dT, shown in Figure 6a (see also Table S1). Assuming that with a larger lattice parameter, the composition is the stoichiometric one and the structural deformation takes place in the cube-like arrangement in the middle of the unit cell, the low lattice parameter can produce defects in the cadmium sub-lattice. The resultant structural deformation does not influence the magnetic behavior, since the affected part of the Cd framework is located far from the uranium atoms (~3.8 Å). Magnetism of UCd₁₁ is likely mediated by the RKKY interactions, which means that the magnetic susceptibility is not influenced by the crystallographic point defects. However, the cubic symmetry of the uranium coordination is locally violated, which leads to reduced peak sharpness in the dM/dT data. The inverse susceptibility data were fit to the Curie–Weiss law. In agreement with previous work,¹⁴ an effective moment μₑffective = 3.43 μ₆ F.U.⁻¹ and Weiss temperature θₜ = −23 K were established.

The antiferromagnetic ordering of UCd₁₁ is also marked by an anomaly in the specific heat data, as shown in Figure 6b. The sharpness of this feature is somewhat reduced compared to some of the previous reports, which can likely be attributed to the polycrystalline nature of the samples. The height and position of the jump are comparable to previous stud-
antiferromagnetic transition, $\gamma = 890 \pm 30 \text{ mJ mol}^{-1} \text{ K}^{-2}$ is similar to previous studies. The antiferromagnetic ordering temperature $T_N = 5 \text{ K}$ does not appear to vary between different UCd$_{11}$ samples. This indicates that magnetism in UCd$_{11}$ is likely rather robust to small changes in crystal features, which is typically not the case for strongly correlated actinide- and lanthanide-based materials.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at [https://pubs.acs.org/doi/10.1021/acs.inorgchem.2c01986](https://pubs.acs.org/doi/10.1021/acs.inorgchem.2c01986).

Crystallographic data are provided in the supporting information (PDF).

### Accession Codes

CCDC 2179377 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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