

Synthesis, structure and physical properties of the new uranium ternary phase $U_3Co_2Ge_7$

Svilen Bobev^{a,*}, Eric D. Bauer^b, Filip Ronning^b, Joe D. Thompson^b, John L. Sarrao^b

^aDepartment of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716, USA

^bMaterials Physics and Applications Division (MPA-10), Los Alamos National Laboratory, Los Alamos, NM 87545, USA

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Abstract

A new ternary compound, $U_3Co_2Ge_7$, has been synthesized from the corresponding elements by a high temperature reaction using molten tin flux. It crystallizes in the orthorhombic $La_3Co_2Sn_7$ -type (Pearson's symbol $oC24$, space group $Cmmm$, No. 65) with lattice parameters determined from single-crystal X-ray diffraction as follows: $a = 4.145(2) \text{ \AA}$; $b = 24.920(7)$; $c = 4.136(2) \text{ \AA}$, $V = 427.2(3) \text{ \AA}^3$. Structure refinements confirm an ordered structure having two crystallographically inequivalent uranium atoms, occupying sites with dissimilar coordination. $U_3Co_2Ge_7$ orders ferromagnetically below 40 K and undergoes a consecutive magnetic transition at 20 K. These results have been obtained from temperature- and field-dependent magnetization, resistivity and heat-capacity measurements. The estimated Sommerfeld coefficient $\gamma = 87 \text{ mJ/mol-U K}^2$ suggests $U_3Co_2Ge_7$ to be a moderately heavy-fermion material.

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1. Introduction

A variety of uranium-containing intermetallic compounds have been extensively studied during the past 3–4 decades [1–6]. The interest in such materials has been largely fueled by the unusual temperature dependence of the specific heat (C_p) that leads to a very large value of C_p/T at low temperature (Sommerfeld coefficient or electronic component to the heat capacity, $\gamma = C_p/T$). Several well-known examples include UPt_3 , UBe_{13} , UGe_2 , UCd_{11} , U_2Zn_{17} , among others, illustrious for the rich heavy-fermion phenomenology they exhibit [7–11]. Today, it is commonly accepted that the anomalously large γ -values in these U -phases arises from hybridization of the $5f$ -electrons with s -, p - and d -electrons of the ligands, resulting in the formation of highly correlated bands near the Fermi level [6,12–14]. Recently, such bands were found to take part in the superconducting condensate as demonstrated on the examples of UGe_2 (itinerant ferromagnet) [7], URu_2Si_2 (hidden order antiferromagnet) [15], $URhGe$ (field-induced

re-entrant superconductor) [16], to name just a few. The latter compound is also regarded as the first bulk ferromagnetic superconductor at ambient pressure. Such unprecedented results have broad implications in various subfields of condensed-matter research and call the attention to new experimental studies to better understand the origin of unconventional superconductivity.

With these ideas in mind, we embarked on exploratory studies of new heavy-fermion materials in the systems $U-TM-Ge$ and $U-TM-Si$, where TM stands for various mid-to-late transition metals. Unlike in previous studies, where arc- or induction-melting has been the synthetic method of choice, we employed the molten metal-flux method [17] in order to grow large single crystals and/or to synthesize metastable phases. With this paper, we report the synthesis, the structural characterization and the properties of a new ferromagnetic compound, $U_3Co_2Ge_7$, which one of the very few U -based phases with the orthorhombic $La_3Co_2Sn_7$ structure type (space group $Cmmm$, No. 65, Pearson's symbol $oC24$) [18,19]. The other two known examples are $U_3Fe_2Si_7$ and $U_3Co_2Si_7$ [20], however, they are incorrectly classified in the Pearson's handbook with their own type (dubbed $U_3Fe_2Si_7$, space group $Cmmm$, No. 65, Pearson's

*Corresponding author. Fax: +1 302 831 6335.

E-mail address: bobev@udel.edu (S. Bobev).

symbol *oC24*) [18]. In spite of this inconsistency in the older literature, these structures are isopointal and are known to have two unique U-sites with very different coordination—one at the center of a cubeoctahedron, analogous to that in UGe_3 (AuCu₃-type), and another one whose polyhedron resembles those of Ce in the orthorhombic CeNiSi₂-type [18]. Temperature- and field-dependent magnetization and resistivity measurements confirm that the 5*f*-electrons of the uranium atoms have neither pure itinerant nor pure localized character. These findings are corroborated by the temperature dependence of the heat capacity, which suggests $\text{U}_3\text{Co}_2\text{Ge}_7$ to be a moderate heavy-fermion compound in the ordered state.

2. Experimental

2.1. Synthesis

The starting materials, all with purity greater than 99.99% were used as received. A mixture of depleted U, Co and Ge in the stoichiometric ratio of 1:1:3 was loaded in an alumina crucible, together with a 20-fold excess of Sn (intended as a flux). The crucible was then placed in a fused silica ampoule, which was subsequently evacuated and flame-sealed. Reactions were carried out in a Lindberg muffle furnace at 1373 K for 4 h, followed by cooling to 873 K at a rate of 5°/h, whereupon the excess tin was removed and the samples were allowed to cool to room temperature. The reaction outcome consisted of thin, plate-like crystals, some up to 3–4 mm³. Later, the majority of these were determined to be of the title compound. Single-crystal diffraction studies also confirmed the presence of $\text{U}_3\text{Co}_4\text{Ge}_7$ [21] as a minor phase.

The crystals of $\text{U}_3\text{Co}_2\text{Ge}_7$ had silver-metallic color. They are stable in air and moisture over periods of time greater than 6 months.

2.2. X-ray diffraction studies

X-ray powder diffraction patterns were taken on a Scintag XDS 2000 diffractometer with monochromatized $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) and up to a 2θ limit of 80°. The collected data were used for a phase identification, which was done using the JADE 6.5 package [22]. The intensity and the peak positions in the experimental powder patterns were in good agreement with those calculated from the structure as refined from single-crystal data (below). However, we point out that assessing the sample purity from powder data could not be considered very reliable. This is easy to understand if one recognizes that many of the Bragg peaks corresponding to $\text{U}_3\text{Co}_2\text{Ge}_7$ and to the side product $\text{U}_3\text{Co}_4\text{Ge}_7$ [21] overlap. Therefore, to ascertain the crystals used for the property measurements, all of them were checked and indexed using X-ray single-crystal diffraction.

Single-crystal X-ray diffraction was also used in order to unequivocally determine the crystal structure. To do so,

several crystals were selected from the Sn-flux reactions, cut to suitable dimensions for data collection and checked for singularity. One of them was subsequently chosen (platelet, $0.04 \times 0.03 \times 0.03 \text{ mm}^3$) for an intensity data collection, which was carried out on a Bruker SMART CCD single-crystal diffractometer with monochromatized $\text{MoK}\alpha$ radiation. Since the crystal was mounted on a glass fiber utilizing Paratone N Oil, a low temperature data acquisition was deemed more appropriate. It was done in 4 batch runs with 0.4° ω -scans, 15 s per frame, $2\theta_{\text{max}} = 56.4^\circ$, covering a full sphere of reciprocal space. The Bruker-supplied SMART and SAINT software packages [23] were used for the data collection, indexing, reduction and integration. Semi-empirical absorption correction based on equivalents was applied with the aid of SADABS [24]. Inspection of the reciprocal space did not provide any evidence for data ($I > 2\sigma(I)$), which violate the reflections' conditions or for twinning.

The structure was solved by direct-methods in *Cmmm* (No. 65) and refined on F^2 with SHELX [25]. At this point, it was recognized that $\text{U}_3\text{Co}_2\text{Ge}_7$ is a new member of the $\text{La}_3\text{Co}_2\text{Sn}_7$ type (Pearson's symbol *oC24*) [18,19], and for the sake of uniformity, the atomic coordinates and the labeling scheme from $\text{La}_3\text{Co}_2\text{Sn}_7$ were adopted (we noted already an inconsistency in the older literature—the $\text{U}_3\text{Fe}_2\text{Si}_7$ and the $\text{U}_3\text{Co}_2\text{Si}_7$ structures [20] are not assigned with the $\text{La}_3\text{Co}_2\text{Sn}_7$ type, although they are isostructural). Refinements of the structure showed no indications that the occupancies of the U, Co, or Ge sites deviate from full—when the site occupation factor of an individual atom was freed to vary while the remaining ones were kept fixed, all deviations from full occupancy were within 3σ . Despite the fact that the $\text{U}_3\text{Co}_2\text{Ge}_7$ crystals were grown in Sn flux, there is no evidence to suggest Sn inclusions or substitutions. This is particularly worth noting because the archetype $\text{La}_3\text{Co}_2\text{Sn}_7$ is a Sn-based compound and excluding $\text{Ce}_3\text{Ni}_2\text{Ge}_7$ [26] there are no other structurally characterized germanides that crystallize with this structure.

In the last refinement cycles, all atoms were refined with anisotropic displacement parameters. The final Fourier map is flat—both the highest residual density and deepest hole (ca. $\pm 3 \text{ e}^-/\text{\AA}^3$) are located approximately 1.5 Å away from Ge4. Additional details of the data collection and structure refinements are given in Table 1. Positional and equivalent isotropic displacement parameters, and relevant interatomic distances are listed in Tables 2 and 3, respectively. Further details on the crystal structure investigations can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, (fax: (49) 7247 808 666; e-mail: crysdta@fiz.karlsruhe.de) on quoting the depository number CSD 418093.

2.3. Physical property measurements

Magnetization measurements were performed in a Quantum Design MPMS-7 SQUID magnetometer from

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