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Ternary rare-earth ruthenium and iridium germanides $RE_3M_2Ge_3$ (RE=Y, Gd–Tm, Lu; M=Ru, Ir)

Anton O. Oliynyk, Stanislav S. Stoyko, Arthur Mar*

Department of Chemistry, University of Alberta, Edmonton, AB, Canada T6G 2G2

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ABSTRACT

Through arc-melting reactions of the elements and annealing at 800 °C, the ternary rare-earth germanides $RE_3Ru_2Ge_3$ and $RE_3Ir_2Ge_3$ have been prepared for most of the smaller RE components (RE=Y, Gd–Tm, Lu). In the iridium-containing reactions, the new phases RE_2IrGe_2 were also generally formed as by-products. Powder X-ray diffraction revealed orthorhombic $Hf_3Ni_2Si_3$-type structures (space group $Cmcm$, Z=4) for $RE_3M_2Ge_3$ (M=Ru, Ir) and monoclinic Sc_2CoSi_2-type structures (space group $C2/m$, Z=4) for RE_2IrGe_2. Full crystal structures were determined by single-crystal X-ray diffraction for all members of $RE_3Ru_2Ge_3$ (a=4.2477(6) Å, b=10.7672(16) Å, c=13.894(2) Å for RE=Y; a=4.2610(3)–4.2045(8) Å, b=10.9103(8)–10.561(2) Å, c=14.0263(10)–13.639(3) Å in the progression of RE from Gd to Lu) and for $Tb_3Ir_2Ge_3$ (a=4.2937(3) Å, b=10.4868(7) Å, c=14.2373(10) Å). Both structures can be described in terms of CrB- and $ThCr_2Si_2$-type slabs built from Ge-centred trigonal prisms. However, band structure calculations on $Y_3Ru_2Ge_3$ support an alternative description for $RE_3M_2Ge_3$ based on $[M_2Ge_3]$ layers built from linked MGe_4 tetrahedra, which emphasizes the strong M–Ge covalent bonds present. The temperature dependence of the electrical resistivity of $RE_3Ru_2Ge_3$ generally indicates metallic behaviour but with low-temperature transitions visible for some members (RE=Gd, Tb, Dy) that are probably associated with magnetic ordering of the RE atoms. Anomalously, $Y_3Ru_2Ge_3$ exhibits semiconductor-like behaviour of uncertain origin. Magnetic measurements on $Dy_3Ru_2Ge_3$ reveal antiferromagnetic ordering at 3 K and several unusual field-dependent transitions suggestive of complex spin reorientation processes.

1. Introduction

A rich variety of ternary rare-earth transition-metal germanides RE–M–Ge are known. Among systems with M=3d metals, the ones involving the later elements (M=Mn, Fe, Co, Ni, Cu) give rise to numerous phases, in contrast to those containing the earlier elements (M=V, Cr) [1,2], for which the new compounds $REMGe_3$ and $RECr_xGe_2$ have only been identified recently [3–5]. The same pattern emerges for systems with M=4d and 5d metals, in which the ones containing the precious metals (M=Ru, Os, Rh, Ir, Pd, Pt) promise to show many phases, whereas those containing the earlier elements have barely been explored [1]. Much of the interest in these germanides relates to their diverse physical properties which may prove useful in materials applications. Recent reports of such germanides containing a precious metal have been motivated by the search for new magnetocaloric (e.g., $GdRu_2Ge_2$) [6], thermoelectric (e.g., $RE_3M_4Ge_{13}$) [7,8], and superconducting materials (e.g., $RE_2Ir_3Ge_5$) [9,10].

We present here the elucidation of the series $RE_3M_2Ge_3$ (RE=Y, Gd–Tm, Lu; M=Ru, Ir). Only a few isolated members of these series have been identified previously: $Ho_3Ru_2Ge_3$ [11–13], $Ho_3Ir_2Ge_3$ [14], and $Lu_3Ir_2Ge_3$ [15]. The crystal structures for all remaining members for the $RE_3Ru_2Ge_3$ series have now been determined, as well as for $Tb_3Ir_2Ge_3$. We report electrical resistivity measurements for the $RE_3Ru_2Ge_3$ series, as well as magnetic susceptibility measurements on $Dy_3Ru_2Ge_3$. The nature of bonding in these compounds has been examined through band structure calculations.

2. Experimental

2.1. Synthesis

Stoichiometric mixtures (0.2-g total mass) of freshly filed RE pieces (RE=Y, Gd–Tm, Lu, 99.9%, Hefa), Ru (99.95%, Cerac) or Ir powder (99.9%, Cerac), and Ge powder (99.9999%, Alfa-Aesar) were pressed into pellets, which were arc-melted in a Centorr 5TA tri-arc furnace on a water-cooled copper hearth under an argon atmosphere. To ensure homogeneity, the samples were

* Corresponding author. Fax: +1 780 492 8231.
E-mail address: arthur.mar@ualberta.ca (A. Mar).

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melted twice, after which the weight loss was found to be less than 1%. The ingots were then sealed within fused-silica tubes and annealed at 800 °C for 12 *d*, followed by quenching in cold water. No attempts were made to extend the *RE* substitution to Yb, whose high volatility would pose problems in arc-melting. The products were characterized by powder X-ray diffraction (XRD) patterns, collected with Cu$K\alpha_1$ radiation on an Inel diffractometer equipped with a curved position-sensitive detector (CPS 120). A summary of the phases identified in the powder XRD patterns is given in Table S1 in Supplementary Data. The Ru-containing samples generally consisted of $RE_3Ru_2Ge_3$ as the major phase (54–100%), along with smaller amounts of RE_2RuGe_2 [16]. The Ir-containing samples generally consisted of $RE_3Ir_2Ge_3$ as the major phase (43–63%), along with RE_2IrGe_2 [15,17] and *RE*IrGe [18,19]. Cell parameters for the orthorhombic $RE_3M_2Ge_3$ (M=Ru, Ir) phases were refined from the powder XRD data with use of the CSD suite of programs [20] and are listed in Table 1. RE_2IrGe_2 were also identified as new phases, which adopt the monoclinic Sc_2CoSi_2-type structure (space group $C2/m$) with refined cell parameters listed in Table 2. (Because Ho_2IrGe_2 and Lu_2IrGe_2 were detected only in trace quantities, their cell parameters could not be refined; Tm_2IrGe_2 did not apparently form.) Small single crystals of $RE_3M_2Ge_3$ (M=Ru, Ir) could be extracted manually from the products and their chemical compositions were determined by energy-dispersive X-ray (EDX) analysis on a JEOL JSM-6010LA scanning electron microscope. The experimental compositions (35–38% *RE*, 24–28% *M*, 36–40% Ge) (Table S2 in Supplementary Data) were in good agreement with expectations (37.5% *RE*, 25.0% *M*, 37.5% Ge).

Table 1
Cell parameters for $RE_3M_2Ge_3$ (M=Ru, Ir).[a]

Compound	*a* (Å)	*b* (Å)	*c* (Å)	*V* (Å^3)	Reference
$Y_3Ru_2Ge_3$	4.2700(9)	10.754(2)	13.877(6)	637.2(5)	This work
$Gd_3Ru_2Ge_3$	4.267(1)	10.962(3)	14.071(4)	658.2(5)	This work
$Tb_3Ru_2Ge_3$	4.2551(7)	10.861(2)	13.981(2)	646.1(3)	This work
$Dy_3Ru_2Ge_3$	4.2529(7)	10.810(2)	13.898(2)	638.9(3)	This work
$Ho_3Ru_2Ge_3$	4.2263(8)	10.729(2)	13.828(2)	627.0(3)	This work
$Ho_3Ru_2Ge_3$	4.242(2)	10.731(6)	13.840(9)	630(1)	[11]
$Er_3Ru_2Ge_3$	4.2263(6)	10.701(1)	13.794(2)	623.8(2)	This work
$Tm_3Ru_2Ge_3$	4.2271(7)	10.661(2)	13.774(3)	620.7(4)	This work
$Lu_3Ru_2Ge_3$	4.2130(8)	10.577(1)	13.676(3)	609.4(3)	This work
$Y_3Ir_2Ge_3$	4.2815(9)	10.448(2)	14.190(3)	634.8(4)	This work
$Gd_3Ir_2Ge_3$	4.321(1)	10.594(2)	14.357(5)	657.2(5)	This work
$Tb_3Ir_2Ge_3$	4.2968(8)	10.521(3)	14.259(4)	644.6(5)	This work
$Dy_3Ir_2Ge_3$	4.290(1)	10.462(3)	14.281(3)	641.0(5)	This work
$Ho_3Ir_2Ge_3$	4.271(1)	10.399(2)	14.100(4)	626.2(4)	This work
$Ho_3Ir_2Ge_3$	4.2730(7)	10.403(1)	14.128(2)	628.0(3)	[14]
$Er_3Ir_2Ge_3$	4.248(1)	10.374(3)	14.179(4)	624.9(5)	This work
$Tm_3Ir_2Ge_3$	4.246(1)	10.324(4)	14.219(4)	623.3(6)	This work
$Lu_3Ir_2Ge_3$	4.2506(7)	10.241(2)	13.945(2)	607.0(3)	This work
$Lu_3Ir_2Ge_3$	4.265(1)	10.191(2)	13.989(4)	608.0(4)	[15]

[a] Cell parameters reported in this work were refined from powder X-ray diffraction data.

Table 2
Cell parameters for RE_2IrGe_2.[a]

Compound	*a* (Å)	*b* (Å)	*c* (Å)	*β* (deg.)	*V* (Å^3)	Reference
Y_2IrGe_2	10.549(3)	4.223(1)	10.256(2)	117.30(1)	406.0(5)	This work
Nd_2IrGe_2	10.84(1)	4.352(1)	10.54(2)	117.23(2)	442(2)	[17]
Gd_2IrGe_2	10.705(2)	4.342(1)	10.197(3)	118.01(2)	418.4(4)	This work
Tb_2IrGe_2	10.677(2)	4.269(1)	10.153(2)	118.19(1)	407.9(3)	This work
Dy_2IrGe_2	10.583(2)	4.268(1)	10.111(2)	118.07(1)	403.0(3)	This work
Er_2IrGe_2	10.513(2)	4.230(1)	10.040(3)	118.10(1)	393.9(3)	This work
Yb_2IrGe_2	10.271(8)	4.228(2)	10.103(9)	116.64(9)	392(1)	[15]

[a] Cell parameters reported in this work were refined from powder X-ray diffraction data.

2.2. Structure determination

Suitable crystals of the entire $RE_3Ru_2Ge_3$ (RE=Y, Gd–Tm, Lu) series were available for single-crystal X-ray diffraction analysis. Crystals of the corresponding $RE_3Ir_2Ge_3$ series were also tested but generally they were too small or diffracted poorly; however, a suitable crystal of one member, $Tb_3Ir_2Ge_3$, gave acceptable results. Intensity data were collected on a Bruker PLATFORM diffractometer equipped with a SMART APEX II CCD area detector and a graphite-monochromated Mo$K\alpha$ radiation source, using ω scans to generate at least 5 sets of frames at different ϕ angles with a frame width of 0.3° and an exposure time of 12 s per frame. All data collections were performed with crystals under nitrogen flow at −100 °C as a matter of routine precaution to minimize sample oxidation and to check for low-temperature structural transitions. Face-indexed absorption corrections were applied. Structure solution and refinement were carried out with use of the SHELXTL (version 6.12) program package [21]. The Laue symmetry indicated an orthorhombic crystal system; systematic absences and intensity statistics established the choice of the centrosymmetric space group *Cmcm*. Direct methods led to a structural model consistent with the $Hf_3Ni_2Si_3$-type structure. Atomic positions were standardized with the program STRUCTURE TIDY [22]. Refinements proceeded in a straightforward fashion, with all atomic sites being fully occupied and having reasonable displacement parameters. Agreement factors were excellent in all cases (conventional $R(F)$ for observed reflections less than 0.05). For two samples, there was some residual electron density in the difference map ($(\Delta\rho)_{max,min}$ = 6.14, −2.05 e$^-$/Å^3 for $Y_3Ru_2Ge_3$ and 6.63, −1.84 e$^-$/Å^3 for $Ho_3Ru_2Ge_3$); however, the peaks were too close (~1.4 Å) to *RE* atoms to be physically meaningful and are likely an artefact of inadequate absorption corrections. Crystal data and further details of the data collections are given in Table 3, final values of the positional and displacement parameters are given in Table 4, and selected interatomic distances are given in Table 5. Further data, in CIF format, have been sent to Fachinformationszentrum Karlsruhe, Abt. PROKA, 76344 Eggenstein-Leopoldshafen, Germany, as supplementary material No. CSD-425769 to –425777 and can be obtained by contacting FIZ (quoting the article details and the corresponding CSD numbers).

2.3. Band structure calculations

Tight-binding linear muffin tin orbital band structure calculations were performed on $Y_3Ru_2Ge_3$ within the local density and atomic spheres approximation with use of the Stuttgart TB-LMTO program [23]. The basis set consisted of Y 5*s*/5*p*/4*d*, Ru 5*s*/5*p*/4*d*, and Ge 4*s*/4*p*/4*d* orbitals, with the Y 5*p* and Ge 4*d* orbitals being downfolded. Integrations in reciprocal space were carried out with an improved tetrahedron method over 129 irreducible *k* points within the first Brillouin zone.

2.4. Electrical resistivity and magnetic susceptibility measurements

The identities of selected single crystals or aggregates of crystals of $RE_3Ru_2Ge_3$ (RE=Y, Gd–Tm, Lu) were confirmed by EDX analysis. Although these samples sometimes exhibited striations that made them unsuitable for X-ray diffraction experiments, they were sufficiently large to permit standard four-probe electrical resistivity measurements to be made between 2 and 300 K on a Quantum Design Physical Property Measurement System (PPMS) equipped with an ac transport controller (Model 7100).