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Antiferromagnetic order in $\text{EuRh}_2(\text{Ga}, \text{In})_8$ V. Fritsch,¹ S. Bobev,¹ N. O. Moreno,¹ Z. Fisk,² J. D. Thompson,¹ and J. L. Sarrao¹¹*Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA*²*Department of Physics, University of California Davis, Davis, California 95616, USA*

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We report the structural, magnetic, thermodynamic, and transport properties of EuRh_2Ga_8 , EuRh_2In_8 , and YbCo_2Ga_8 . While the two former compounds show the onset of antiferromagnetic order at 20 and 5 K respectively, the latter remains nonmagnetic down to lowest temperatures. The electrical resistivity of the magnetic Eu-compounds is nearly unaffected by an external magnetic field, but the nonmagnetic YbCo_2Ga_8 develops a positive magnetoresistance.

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After the discovery of superconductivity in the heavy fermion system CeRhIn_5 (Ref. 1), many structurally related systems have been studied.^{2–4} Many europium and ytterbium intermetallic compounds display ground state properties similar to their more heavily studied cerium counterparts.⁵ Thus, we attempted to synthesize $\text{EuT}(\text{Ga}, \text{In})_5$ and $\text{YbT}(\text{Ga}, \text{In})_5$, with $\text{T}=\text{Co}, \text{Rh}, \text{Ir}$. Here we report one outgrowth of these efforts, the synthesis and characterization of YbCo_2Ga_8 , EuRh_2Ga_8 , and EuRh_2In_8 . As discussed below, the observed physical properties are consistent with divalent Eu and Yb.

Large single crystals of YbCo_2Ga_8 , EuRh_2Ga_8 , and EuRh_2In_8 were initially identified as the major products of reactions loaded with the intention to produce YbCoGa_5 , EuRhGa_5 , and EuRhIn_5 . Eu or Yb, and Rh or Co with the desired stoichiometric ratios, were combined with 50-fold excess of low-melting Ga or In, which serve as a crystal growth media. Reactions were carried out in quartz-encapsulated alumina crucibles using the temperature profile: quick ramp (250°C/h) to 1175°C, dwell for 5 h, slow cool (–10°C/h) to 500°C. At that point, the molten Ga (or In) was removed by centrifugation. Rod-like crystals (up to ca. 5–8 mm) with silver-metallic luster were isolated and used for the structure determination work and for the physical properties measurements. In contrast, under similar synthetic conditions, Eu-Co-Ga and Yb-Rh-Ga mixtures do not form EuCo_2Ga_8 and YbRh_2Ga_8 . Rather, the former yields EuGa_4 (Ref. 6) and CoGa_3 , while the latter produces crystals of $\text{Yb}_2\text{Rh}_3\text{Ga}_9$ (Ref. 7). Finally, Yb-Rh-In reactions yield YbRhIn_5 .

X-ray powder diffraction patterns of crushed crystals of YbCo_2Ga_8 , EuRh_2Ga_8 , and EuRh_2In_8 were compared with theoretically calculated ones, and both the peak positions and the intensities were in excellent agreement. The crystal structures of YbCo_2Ga_8 and EuRh_2In_8 have been previously reported.^{8,9} All three compounds are isostructural and crystallize with the orthorhombic CaCo_2Al_8 -type (Pearson's code *oP44*). Here, we report a single-crystal structure determination for EuRh_2Ga_8 .

Intensity data were collected at 90(3)K on a Bruker SMART 1000 CCD diffractometer equipped with a CRYO COOLER low-temperature apparatus. A hemisphere of data was collected using graphite monochromatized Mo K α ra-

diation ($0.3^\circ \omega$ -scans, $2\theta_{\text{max}} \sim 63^\circ$) for a bar-like, silver-metallic crystal of EuRh_2Ga_8 (crystal size $0.09 \times 0.07 \times 0.06$ mm; $T_{\text{min}}/T_{\text{max}} = 0.1223/0.1961$, 6796 total reflections, 1352 unique reflections, $R_{\text{int}} = 4.44\%$). The data were corrected for Lorentz and polarization effects and merged in Laue symmetry *mmm* using the SMART and SAINT software.¹⁰ Multiscan absorption correction was applied with the SADABS software package. Data were subsequently refined on F^2 (data to parameter ratio greater than 13) with the aid of the SHELXTL v5.10 package.¹¹ All atoms are refined with anisotropic displacement parameters. Selected data collection and structure refinement parameters are given in Table I.¹²

There are twelve crystallographically unique positions in the EuRh_2Ga_8 structure – one Eu, two Rh's, and nine Ga's (Table II). All atoms are in special positions and are situated on mirror planes at $z=0$ and $z=1/2$. Comprehensive structure description has been given elsewhere;^{8,9} here, we discuss details of the Eu- and Rh-first coordination spheres. The Eu atoms center pentagonal prisms formed by ten nearest Ga atoms at distances from 3.1140(7) to 3.2020(9) Å [Fig. 1(b)].

TABLE I. Selected data collection and refinement parameters for EuRh_2Ga_8 .

Empirical formula	EuRh_2Ga_8
Formula weight	915.54
Space group, Z	<i>Pbam</i> (No. 55), 4
Radiation, λ (Å)	Mo K α , 0.71073
Temperature (K)	90(3)
Unit cell parameters:	
a (Å)	14.6577(12)
b (Å)	12.5677(10)
c (Å)	4.1073(3)
V (Å ³)	756.62(10)
μ (cm ^{–1})	402.74
ρ_{calc} (g/cm ³)	8.037
R_1/wR_2^a (%), $I > 2\sigma_I$	2.88/6.04
R_1/wR_2 (%), all data	4.53/6.77

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = (\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2])^{1/2}$, where: $w = 1/[\sigma^2 F_o^2 + (A \cdot P) + B \cdot P]$; A and B are weight coefficients, $P = (F_o^2 + 2F_c^2)/3$.

TABLE II. Atomic coordinates and equivalent isotropic displacement parameters (U_{eq}) for EuRh_2Ga_8 .

Atom	Site	x	y	z	$U_{eq}(\text{\AA}^2)^a$
Eu(1)	4h	0.68044(3)	0.15557(3)	1/2	0.0029(1)
Rh(1)	4h	0.90443(5)	0.34519(5)	1/2	0.0018(1)
Rh(2)	4h	0.59655(5)	0.34519(5)	1/2	0.0021(1)
Ga(1)	2a	0	0	0	0.0033(3)
Ga(2)	2d	0	1/2	1/2	0.0053(3)
Ga(3)	4g	0.12317(7)	0.16712(7)	0	0.0053(3)
Ga(4)	4g	0.31456(7)	0.45045(7)	0	0.0031(2)
Ga(5)	4g	0.32272(6)	0.24223(7)	0	0.0035(2)
Ga(6)	4g	0.01332(7)	0.32949(7)	0	0.0034(2)
Ga(7)	4g	0.36681(7)	0.02235(7)	0	0.0028(2)
Ga(8)	4h	0.95662(7)	0.15956(7)	1/2	0.0041(2)
Ga(9)	4h	0.74737(7)	0.39857(7)	1/2	0.0043(2)

^a U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

The five rectangular faces of the Ga_{10} -prisms are capped by five other Ga atoms at distances ranging from 3.208(1) to 4.048(1) Å. The five side-edges of the prisms in turn are capped by five Rh atoms with Eu-Rh bond distances in the narrow range of 4.0457(9) to 4.0943(8) Å. These 15 Ga's and 5 Rh's next nearest neighbors of each Eu form a rather symmetrical "encapsulation" around it. The two independent Rh positions have quite similar coordination by nine adjacent Ga's [Fig. 1(b)] with Rh-Ga bond distances from 2.365(1) to 2.7005(7) Å. Thus, the structure can be viewed as built of fused polyhedra of Ga that are interstitially stabilized by rare-earth and transition metal, and the latter play an important role in templating the structure. This observation is supported by the fact that in recently reported refinements of the structures of CeRu_2Ga_8 and NdRu_2Ga_8 , the Ru sites are nearly 90% occupied, and the Ru occupation factor apparently increases with increasing the size of the rare-earth element.¹³ In EuRh_2Ga_8 on the other hand, all atoms are fully occupied with deviations from the ideal values of less than 2 (full occupancy was confirmed by freeing the site occupation factors for an individual atom, while the remaining atoms were kept with fixed occupancies). The packing requirements of the above-described polyhedral cages could perhaps explain why most of the members of the "1-2-8" family are based on early (larger atomic radii) lanthanides and divalent Eu and Yb.

The dc magnetic susceptibility $\chi(T) = M/H$ measurements were performed in a Quantum Design superconductor quantum interference device magnetometer in fields of 1 kOe. The resistivity was measured with a conventional four-probe method in a home-build He⁴-cryostat as was the specific heat, using a thermal relaxation technique. Measurements of the resistivity and specific heat in a magnetic field were performed in a Quantum Design physical properties measurement system (PPMS).

The results of the resistivity measurements are shown in Fig. 2. The magnetic field was applied perpendicular to the c -axis, while the current ran along it. The main frame depicts

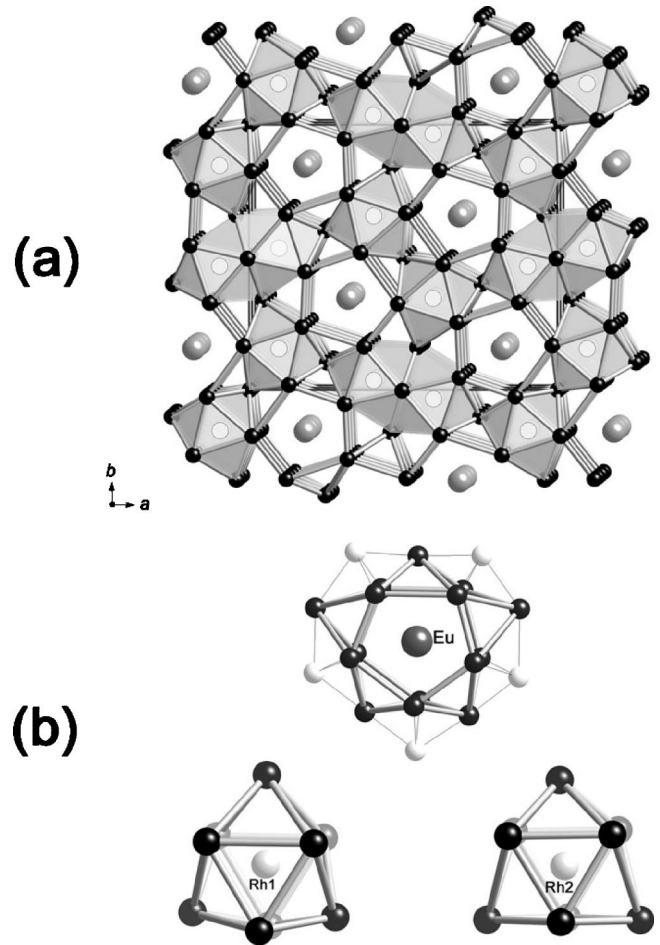


FIG. 1. (a) Ball-and-stick representation of the orthorhombic structure of EuRh_2Ga_8 down the c -axis. (b) Coordination environments for the Eu and the two crystallographically different Rh sites. On all drawings, Ga atoms are shown as small black spheres, Rh atoms as small light spheres, and the Eu atoms are shown as large gray spheres.

the resistivities of YbCo_2Ga_8 , EuRh_2Ga_8 , and EuRh_2In_8 in the temperature range from 1.3 to 300 K in zero field and in $H=1$ kOe. In the high-temperature region above ≈ 100 K they exhibit a linear temperature dependence, as expected for metals. In this temperature regime no significant magnetoresistance is observed. The insets of Fig. 2 enlarge the low-temperature resistivities. EuRh_2In_8 shows a linear temperature dependence down to a superconducting transition at $T_C=3.4$ K due to residual In-flux that is suppressed in small applied fields. The resistivity of EuRh_2Ga_8 has a kink at $T=20$ K and drops down steeply below 4 K. While the first transition at $T=20$ K is not affected by an external magnetic field the second transition below $T=4$ K is slightly shifted to lower temperatures. The resistivity of YbCo_2Ga_8 develops a plateau below 15 K and a superconducting transition at 1.5 K, due to Ga-flux. In a magnetic field the resistivity departs from the zero field measurement at temperatures below $T \approx 100$ K. The low-T magnetoresistance is shown in more detail below.

Figure 3 presents the magnetic susceptibility of EuRh_2Ga_8 , EuRh_2In_8 , and YbCo_2Ga_8 . YbCo_2Ga_8 shows only

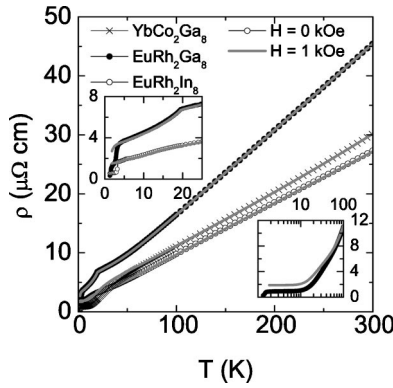


FIG. 2. Resistivity of YbCo_2Ga_8 , EuRh_2Ga_8 , and EuRh_2In_8 in zero field and in a field $H=1$ kOe. Upper Inset: low-temperature region of the resistivity of EuRh_2Ga_8 and EuRh_2In_8 . Lower Inset: low-temperature region of the resistivity of YbCo_2Ga_8 .

a weak temperature dependence. The small increase at low temperatures is likely due to paramagnetic impurities. The inverse susceptibility of EuRh_2In_8 (EuRh_2Ga_8) varies linearly with temperature above 6 K (20 K), obeying a Curie-Weiss law. The Weiss temperature is $\theta = -6.2$ K (-2.5 K) and the paramagnetic moment $\mu = 8.07 \mu_B$ ($7.80 \mu_B$), near the expected value for Eu^{2+} of $7.93 \mu_B$. At 5 K the onset of antiferromagnetic order is observed in EuRh_2In_8 . At $T = 20$ K EuRh_2Ga_8 displays the onset of antiferromagnetic order, which is still visible in an external magnetic field $H = 50$ kOe, as shown in the inset of Fig. 3. At $T = 8$ K a second transition is observed. This lower transition, likely due to a

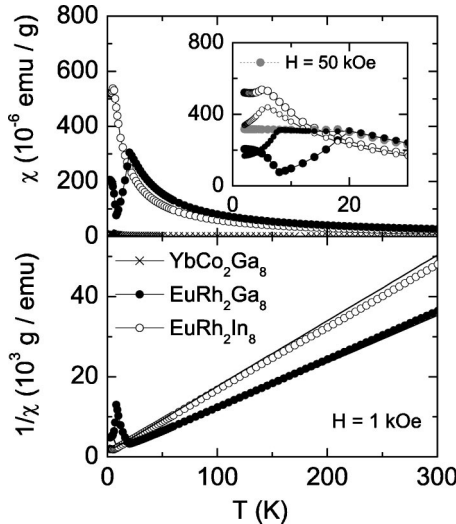


FIG. 3. Upper panel: susceptibility of EuRh_2Ga_8 (solid circles), EuRh_2In_8 (open circles), and YbCo_2Ga_8 (crosses). Inset: low-temperature region of the susceptibility of EuRh_2Ga_8 in a magnetic field of 0 kOe (solid circles) and 50 kOe (gray circles) and EuRh_2In_8 without a magnetic field (open circles). The field was applied along the c -axis (larger symbols) and perpendicular to the c -axis (smaller symbols). Lower panel: inverse susceptibility of EuRh_2Ga_8 (solid circles) and EuRh_2In_8 (open circles). The field was applied along the c -axis. The solid lines represent measurements with the field applied perpendicular to the c -axis.

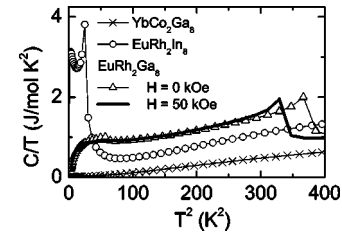


FIG. 4. Specific heat of EuRh_2Ga_8 (triangles), EuRh_2In_8 (circles), and YbCo_2Ga_8 (crosses). The solid line represents the specific heat of EuRh_2Ga_8 in an external field of 50 kOe.

reordering of spins, vanishes in an external magnetic field. No significant magnetic anisotropy is observed in EuRh_2In_8 or EuRh_2Ga_8 . In the In-compound the susceptibility for $H \perp c$ is slightly lower than for $H \parallel c$, likely due to demagnetization effects. In the Ga-compound the susceptibility for $H \parallel c$ decreases at the first transition at $T = 20$ K while for $H \perp c$ the susceptibility is unchanged, suggesting that the ordered moments are oriented parallel to the c -axis. The above mentioned reordering of the spins at $T = 8$ K is clearly observable in both measurements.

In Fig. 4 results of specific heat measurements are shown as C/T versus T^2 . YbCo_2Ga_8 is expected to exhibit a linear temperature dependence in this representation. However, its specific heat shows strong deviations from linearity, indicating a very low Debye temperature, which makes its determination and the determination of the Sommerfeld coefficient difficult. The specific heat data of EuRh_2In_8 confirm the onset of antiferromagnetic order at $T_N = 5$ K, as observed in susceptibility and resistivity data. This peak in the specific heat is followed by a second broader anomaly at 1.6 K, probably due to a reordering of the spins. EuRh_2Ga_8 exhibits a peak at 19 K, coinciding with the anomalies in susceptibility and resistivity, indicating the onset of antiferromagnetic order. Below $T = 8$ K a broad anomaly is observed in the specific heat, indicating a second magnetic transition in analogy to the In-compound. An external magnetic field of 50 kOe shifts the peak at 19 K to lower temperatures, as expected for an antiferromagnetic transition. The second transition is suppressed by the magnetic field. A similar anomaly, observed in ferromagnetic EuB_6 , was suppressed in a magnetic field as well.¹⁴ This suggests that the unusual shapes of these second transitions can be attributed to peculiarities in the exchange interaction in the ordered state and to the presence of small crystal field splitting.¹⁴⁻¹⁶

To obtain the magnetic contribution to the specific heat of the Eu-compounds we scaled the specific heat of the isostructural non-magnetic YbCo_2Ga_8 with the quotient of square root of the molecular masses and subtracted the result from the specific heat of the corresponding Eu-compound. From the magnetic contribution of C/T we calculated the magnetic entropy of EuRh_2Ga_8 and EuRh_2In_8 (not shown). Eu^{2+} has $S = 7/2$ and thus for the magnetic entropy a value $S_m = R \ln(2S+1) = 17.3$ J/mol K is expected. About 85% of this value is reached at the respective Néel temperatures.

As mentioned above, YbCo_2Ga_8 develops a magnetoresistance at low temperatures. Since the current was applied perpendicular to the magnetic field, we measured a full hysteresis

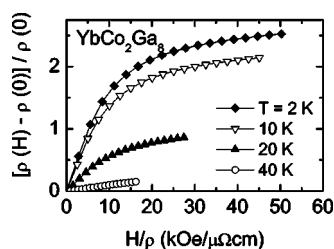


FIG. 5. Kohler plot of the magnetoresistance of YbCo_2Ga_8 .

esis loop (not shown) to exclude Hall effects. In Fig. 5 the magnetoresistance is depicted in the so-called Kohler plot.¹⁷ YbCo_2Ga_8 does not obey Kohler's rule. Since Kohler's rule fails even in simple metals like In or Al,¹⁸ due to band structure and Fermi surface effects, it is no surprise that it fails in YbCo_2Ga_8 . However, a positive magnetoresistance is suggestive of a nonmagnetic rare-earth configuration, as in $\text{RENi}_2\text{B}_2\text{C}$,¹⁹ further confirming Yb's divalent configuration in YbCo_2Ga_8 . The magnitude of the magnetoresistance in YbCo_2Ga_8 is comparable to that observed in pure In or Al.

The general question raised by our study is why do the studied compounds crystallize in the orthorhombic 128 stoichiometry and not the more widely known 115 and 218 stoichiometry, as for the well-known Ce-based variants.²⁰ The first answer is the valence of the rare-earth ion: In the

115s as well as in the 218s the RE-ion, namely, Ce, is trivalent and in a f^1 -state. In EuRh_2Ga_8 and EuRh_2In_8 as well as in YbCo_2Ga_8 , Eu and Yb are divalent, resulting in the 128-structure of CaCo_2Al_8 with the divalent Ca on the RE-site. There do exist Ce-based 128-systems such as CeM_2X_8 with $\text{M}=\text{Fe}, \text{Co}$ and $\text{X}=\text{Al}, \text{Ga}$.²¹⁻²³ In these systems, depending on the elements M and X, a transition from a magnetic, trivalent state of Ce in the case of CeCo_2Ga_8 to a nonmagnetic Kondo-lattice CeCo_2Al_8 is found, followed by CeFe_2Al_8 with Ce in a mixed valence state.²¹ This leads to the conclusion that the smaller Al-lattice drives the Ce from the bigger trivalent state into the smaller mixed-valent/tetravalent state.

In summary, we investigated the ternary compounds EuRh_2Ga_8 and EuRh_2In_8 as well as their nonmagnetic analog YbCo_2Ga_8 . The occurrence of antiferromagnetic order in both Eu-compounds at $T_N=20$ K and $T_N=5$ K, respectively, was confirmed by susceptibility and specific heat measurements and was corroborated by resistivity measurements. Evidence for a lower-temperature spin reconfiguration was also seen in both compounds. As expected no magnetic order was found in YbCo_2Ga_8 .

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¹²Full details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany [fax: (+49) 7247-808-666

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