ELSEVIER

Journal of Alloys and Compounds 239 (1996) 34–40

Journal of
ALLOYS
AND COMPOUNDS

Ternary germanides LnAgGe (Ln = Y, Sm, Gd–Lu) with ordered Fe_2P-type structure

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Received 2 January 1996

Abstract

The title compounds were prepared from the elements by arc-melting and subsequent annealing at 970 K. They crystallize with the hexagonal ZrNiAl-type structure, a ternary ordered variant of the well known Fe_2P type. The structures of GdAgGe, DyAgGe and ErAgGe (all space group $P\bar{6}2m$) have been refined from single-crystal X-ray diffractometer data: a = 715.4(2) pm, c = 423.7(1) pm, $wR2$ = 0.0467, 249 F^2 values and 14 variables for GdAgGe; a = 710.67(7) pm, c = 419.73(5) pm, $wR2$ = 0.0463, 245 F^2 values and 14 variables for DyAgGe; a = 706.34(3) pm, c = 416.87(2) pm, $wR2$ = 0.0514, 279 F^2 values and 14 variables for ErAgGe respectively. The structures contain two crystallographically different germanium positions. Both of them are located in tricapped trigonal prisms: $[Ge1Ln_6Ag_3]$ and $[Ge2Ag_6Ln_3]$. Magnetic susceptibility measurements show antiferromagnetic ordering at Néel temperatures of 13.0(2) and 3.3(1) K for GdAgGe and ErAgGe respectively. DyAgGe shows ferromagnetic ordering at T_C = 14.0(2) K. The experimentally determined magnetic moments at high temperature compare well with those expected for the free Ln^{3+} ions. The latter three germanides are metallic conductors.

Keywords: Rare earth silver germanium; ZrNiAl-structure; Antiferromagnetism; Metallic conductivity

1. Introduction

In recent years the ternary intermetallic compounds LnTX with Ln = rare earth metals, T = late transition metals and X = elements of the p block have attracted much interest because of their greatly varying structural and physical properties. Today, more than 1000 intermetallic compounds with the simple 1:1:1 composition are known [1]. An overview of this large family of compounds which crystallize in more than 30 different structure types was given recently by Fornasini and Merlo [2]. A detailed review of the magnetic and electrical properties of these fascinating compounds was published by Szytula and Leciejewicz [3].

Recently, we reported on the crystal and electronic structures of the LnAuGe series [4–7]. These germanides crystallize in ternary ordered variants of the $CaIn_2$ structure (NdPtSb and LiGaGe type) and show a transition from two- to three-dimensional [AuGe] polyanions, depending on the size of the rare earth metal atom [5]. We have now extended our investigations to the corresponding systems with silver as transition metal component. In the literature only powder investigations on some LnAgGe intermetallics are given [8,9]. Here we report on the synthesis, single crystal structure refinements and physical properties of the series LnAgGe (Ln = Y, Sm, Gd–Lu). In contrast to the gold compounds which all crystallize in the ordered $CaIn_2$ type, the equiatomic rare earth metal–silver–germanides adopt different structure types. While the compounds with early rare earth metals (Ln = La–Nd) also adopt the NdPtSb structure [8], those with Ln = Y, Sm and Gd–Lu crystallize with the ZrNiAl structure, a ternary ordered variant of Fe_2P.

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PII S0925-8388(96)02201-3

EuAgGe contains divalent europium and adopts the structure of $CeCu_2$ [10].

2. Experimental

Starting materials for the preparation of the germanides were dentritic lumps of the rare earth metals (Johnson Matthey), silver wire (Degussa, diam. 2.0 mm) and germanium lumps (Wacker), all with stated purities better than 99.9%. In the first step, small pieces of the dentritic rare earth metal lumps were melted under argon in an arc-melting furnace. The argon was purified over molecular sieves, titanium sponge (at 900 K) and an oxisorb catalyst [11]. In the second step, the rare earth pellets were reacted together with the silver wire and germanium lumps in the ideal atomic ratio. The resulting buttons were turned around and remelted three times on each side to ensure homogeneity. The weight losses after several meltings were always smaller than 1%. The samples were subsequently sealed in evacuated silica tubes and annealed at 970 K for ten days.

The samples were characterized after arc-melting and also after the annealing process by taking powder patterns (modified Guinier technique [12]) with Cu $K\alpha_1$ radiation and 5N silicon ($a = 543.07$ pm) as internal standard. The indexing of the diffraction lines was ensured by intensity calculations [13] using the positional parameters of the refined structures. The lattice constants (Table 1) were obtained by least-squares refinements of the Guinier powder data. They are in good agreement with the data published earlier by Zanicchi et al. [9] for GdAgGe, DyAgGe, ErAgGe and YbAgGe.

Table 2
Magnetic properties of GdAgGe, DyAgGe and ErAgGe

Compound	$T_{C,N}$ [K]	θ [K]	$\mu_{exp}(Ln^{3+})$ [μ_B]	$\mu_{eff}(Ln^{3+})$ [μ_B]
GdAgGe	13.0(2)	−23(1)	7.7(1)	7.94
DyAgGe	14.0(2)	−11(1)	10.3(1)	10.63
ErAgGe	3.3(1)	−1(1)	9.1(1)	9.58

Single-crystal intensity data were collected using a four-circle diffractometer (CAD4) with graphite monochromatized Ag $K\alpha$ radiation and a scintillation counter with pulse height discrimination.

The magnetic susceptibilities of polycrystalline pieces were determined with a SQUID magnetometer (Quantum Design, Inc.) between 4.2 and 300 K with a magnetic flux density of 0.1 T.

The specific resistivities were measured on small blocks ($1.0 \times 1.5 \times 2.5$ mm^3 for GdAgGe, $1.0 \times 1.5 \times 2.1$ mm^3 for DyAgGe and $0.6 \times 0.8 \times 1.2$ mm^3 for ErAgGe) with a conventional four-probe technique. The cooling and heating curves measured between 4.2 and 300 K were identical within error limits.

3. Results and discussion

3.1. Structure refinements and crystal chemistry

Needle shaped single crystals of the gadolinium, dysprosium and erbium compounds could easily be isolated from the crushed samples prepared by arc-melting. They were examined by Buerger precession photographs to establish both symmetry and suitability for intensity data collection. The crystals were oriented with the needle axes perpendicular to the X-ray beam, and the axis turned out to be the short one, as is

Table 1
Lattice constants of the hexagonal germanides with ordered Fe_2P structure (standard deviations in parentheses)

Compound	a (pm)	c (pm)	c/a	V (nm^3)	Ref.
YAgGe	711.80(6)	419.68(4)	0.590	0.1841(1)	This work
SmAgGe	720.05(9)	426.92(7)	0.593	0.1917(1)	This work
GdAgGe	715.4(2)	423.7(1)	0.592	0.1878(2)	This work
GdAgGe[a]	716.54(6)	423.41(3)	0.591	0.1883(3)	This work
GdAgGe	716.4	424.1	0.592	0.1885	[9]
TbAgGe	712.77(13)	421.03(9)	0.591	0.1852(1)	This work
DyAgGe	710.67(7)	419.73(5)	0.591	0.1836(1)	This work
DyAgGe[a]	710.56(8)	419.60(4)	0.591	0.1835(1)	This work
DyAgGe	710.5	419.8	0.591	0.1835	[9]
HoAgGe	707.83(8)	418.26(6)	0.591	0.1815(1)	This work
ErAgGe	706.34(3)	416.87(2)	0.590	0.1801(1)	This work
ErAgGe[a]	706.49(4)	416.65(1)	0.590	0.1808(2)	This work
ErAgGe	706.3	417.4	0.591	0.1803	[9]
TmAgGe	704.15(5)	415.70(4)	0.590	0.1785(1)	This work
YbAgGe	705.24(11)	413.87(8)	0.587	0.1783(1)	This work
YbAgGe	705.9	414.7	0.587	0.1790(1)	[9]
LuAgGe	701.25(9)	413.37(7)	0.589	0.1760(1)	This work

[a] These values were obtained from high-angle reflections on the four-circle diffractometer.

usually the case. The precession photographs showed hexagonal symmetry and no systematic extinctions. The structure refinements confirmed the non-centrosymmetric space group $P\bar{6}2m$, in agreement with previous investigations [9,14]. Some crystallographic data and experimental details for the data collections are listed in Table 3.

The atomic parameters of ScRuGe [14] were taken as starting values and the structures were refined by full-matrix least-squares cycles using SHELXL-93 [15], with anisotropic atomic displacement parameters for all atoms. The structures of DyAgGe and ErAgGe refined instantly to the residuals listed in Table 3. In the refinement of the GdAgGe structure the Flack parameter [16,17] indicated that the crystal investigated had the other absolute structure. We therefore inverted the atomic parameters and refined the structure again. Final difference Fourier analyses revealed no significant residual peaks in all three refinements. Atomic coordinates and interatomic distances are listed in Tables 4 and 5.

Ten ternary germanides LnAgGe (Ln = Y, Sm, Gd–

Table 3
Crystal data and structure refinement for GdAgGe, DyAgGe and ErAgGe

Empirical formula	GdAgGe	DyAgGe	ErAgGe
Formula weight (g mol^{-1})	337.71	342.96	347.72
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (pm)	56.086	56.086	56.086
Crystal system	hexagonal	hexagonal	hexagonal
Space group	$P\bar{6}2m$ (No. 189)	$P\bar{6}2m$ (No. 189)	$P\bar{6}2m$ (No. 189)
Unit cell dimensions	see Table 1	see Table 1	see Table 1
Formula units per cell	$Z = 3$	$Z = 3$	$Z = 3$
Calculated density (g cm^{-3})	8.96	9.31	9.62
Crystal size (μm^3)	40 × 50 × 270	35 × 35 × 200	50 × 50 × 325
Absorption correction	from ψ-scan data	from ψ-scan data	from ψ-scan data
Transmission ratio (max/min)	1:0.869	1:0.707	1:0.671
Absorption coefficient (mm^{-1})	24.12	26.52	29.11
$F(000)$	429	435	441
θ range for data collection	2° to 24°	2° to 24°	2° to 26°
Scan type	ω/θ	ω/θ	ω/θ
Range in hkl	$+10; -10 \leq k \leq 8; \pm 6$	$\pm 10; \pm 10; \pm 6$	$-8 \leq h \leq 10; -10 \leq k \leq 9; \pm 6$
Total no. reflections	1257	1720	1415
Independent reflections	249 ($R_{int} = 0.0273$)	245 ($R_{int} = 0.0439$)	279 ($R_{int} = 0.0839$)
Data/restraints/parameters	249/0/14	245/0/14	279/0/14
Goodness-of-fit on F^2	1.447	1.567	1.258
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0201$, $wR2 = 0.0467$	$R1 = 0.0203$, $wR2 = 0.0463$	$R1 = 0.0215$, $wR2 = 0.0514$
R indices (all data)	$R1 = 0.0203$, $wR2 = 0.0467$	$R1 = 0.0203$, $wR2 = 0.0463$	$R1 = 0.0215$, $wR2 = 0.0514$
Extinction coefficient	0.092(5)	0.112(6)	0.137(7)
Absolute str. parameter	−0.02(4)	0.00(4)	0.00(3)
Largest diff. peak and hole (e nm^{-3})	1992 and −3015	2506 and −3000	3031 and −2625

Table 4
Atomic coordinates and anisotropic displacement parameters (pm^2) for GdAgGe, DyAgGe and ErAgGe (all space group $P\bar{6}2m$)

Atom	Wyckoff site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{eq}
GdAgGe									
Gd	3f	0.41674(7)	0	0	58(2)	48(2)	69(2)	24(1)	59(2)
Ag	3g	0.75131(11)	0	1/2	75(3)	87(4)	120(4)	43(2)	92(2)
Ge1	2d	2/3	1/3	1/2	54(4)	54(4)	64(5)	27(2)	57(3)
Ge2	1a	0	0	0	67(5)	67(5)	94(8)	34(2)	76(4)
DyAgGe									
Dy	3f	0.58268(7)	0	0	78(2)	67(2)	71(3)	34(1)	73(2)
Ag	3g	0.24925(11)	0	1/2	89(3)	99(4)	121(3)	50(2)	102(2)
Ge1	2d	1/3	2/3	1/2	75(4)	75(4)	64(5)	37(2)	71(3)
Ge2	1a	0	0	0	87(5)	87(5)	99(7)	44(2)	91(3)
ErAgGe									
Er	3f	0.58250(7)	0	0	75(2)	64(2)	69(2)	32(1)	71(2)
Ag	3g	0.24980(12)	0	1/2	88(3)	104(4)	123(3)	52(2)	104(2)
Ge1	2d	1/3	2/3	1/2	75(4)	75(4)	73(5)	37(2)	74(3)
Ge2	1a	0	0	0	87(5)	87(5)	92(7)	43(2)	89(3)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. The anisotropic displacement factor exponent takes the form: $-2\pi^2[(ha^*)^2U_{11} + \cdots + 2kha^*b^*U_{12}]$. $U_{13} = U_{23} = 0$.

Table 5
Interatomic distances (pm) calculated with the powder lattice constants in the structures of GdAgGe, DyAgGe and ErAgGe. Standard deviations are equal to or less than 0.1 pm

GdAgGe				DyAgGe				ErAgGe			
Gd:	1	Ge2	298.1	Dy:	1	Ge2	296.6	Er:	1	Ge2	294.9
	4	Ge1	301.8		4	Ge1	299.3		4	Ge1	297.3
	2	Ag	319.6		2	Ag	316.5		2	Ag	314.1
	4	Ag	335.2		4	Ag	332.9		4	Ag	330.9
	4	Gd	372.3		4	Dy	369.6		4	Er	367.3
	2	Gd	423.7		2	Dy	419.7		2	Er	416.9
Ag:	2	Ge1	273.8	Ag:	2	Ge1	271.1	Ag:	2	Ge1	269.8
	2	Ge2	276.6		2	Ge2	274.6		2	Ge2	273.1
	2	Ag	308.1		2	Ag	306.8		2	Ag	305.6
	2	Gd	319.6		2	Dy	316.5		2	Er	314.1
	4	Gd	335.2		4	Dy	332.9		4	Er	330.9
Ge1	3	Ag	273.8	Ge1:	3	Ag	271.7	Ge1:	3	AG	269.8
	6	Gd	301.8		6	Dy	299.3		6	Er	297.3
Ge2:	6	Ag	276.6	Ge2:	6	Ag	274.6	Ge2:	6	Ag	273.1
	3	Gd	298.1		3	Dy	296.6		3	Er	294.9

Lu), six for the first time, have been prepared and investigated by X-ray diffraction on both powder and single-crystals. The cell volumes of the hexagonal germanides are plotted in Fig. 1 as a function of the rare earth element. They decrease monotonically from the Sm to the Lu compound, as was expected from the lanthanoid contraction. The cell volume of the yttrium compound lies between the volumes of the terbium and dysprosium compounds, as is frequently observed for such intermetallic compounds [18–20]. In agreement with the powder data of Zanicchi et al. [9], the ytterbium compound shows a small positive deviation from the smooth curve (see Fig. 1), possibly indicating partial divalent ytterbium in YbAgGe.

The powder patterns of the germanides could easily be indexed on the basis of hexagonal unit cells with intensity sequences resembling the ZrNiAl-type structure [21,22], a ternary ordered version of the Fe_2P type [23]. As already discussed in detail by Hovestreydt et al. [14], there is a site occupancy problem for compounds with ordered Fe_2P structure.

In the ordered Fe_2P structure (ZrNiAl-type), the transition metal and p element atoms can occupy a tetrahedral (Fe1 position in Fe_2P) or the trigonal prismatic sites (P1 and P2 positions in Fe_2P), while the rare earth atoms always occupy the Fe2 position. In order to clarify this problem, single crystal data of the present LnAgGe intermetallics were desirable. The structure refinements of the gadolinium, dysprosium and erbium compounds unambiguously showed that the silver atoms occupy the tetrahedral site, while the two trigonal prismatic sites are occupied by the germanium atoms.

A projection of the DyAgGe structure is shown in Fig. 2. The two different tricapped trigonal prismatic sites, i.e. $[Ge1Dy_6Ag_3]$ and $[Ge2Ag_6Dy_3]$, are outlined. The dysprosium atoms have coordination number (CN) 17, with six dysprosium, six silver and five germanium atoms forming the coordination polyhedron. The five germanium neighbours build a tetragonal pyramid around the dysprosium atom, while the six silver neighbours form an elongated trigonal prism.

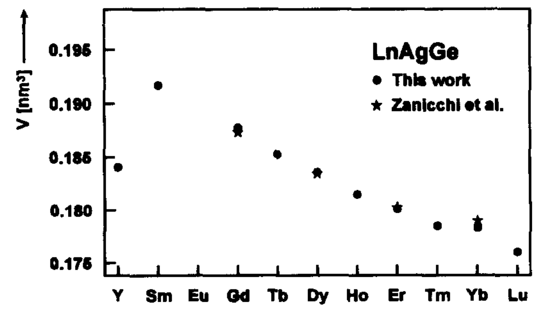

Fig. 1. Plot of the cell volumes of the germanides with ordered Fe_2P-type structure. The size of the dots corresponds approximately to the standard deviations.

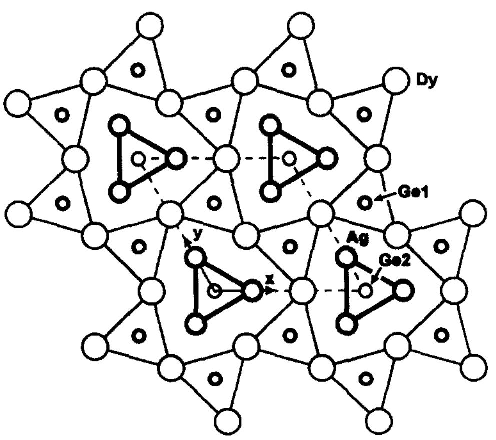

Fig. 2. Crystal structure of DyAgGe projected onto the xy plane. All atoms lie on mirror planes at $z = 0$ and $z = 1/2$, indicated by thin and thick lines respectively. The trigonal prisms around the germanium atoms are outlined.

The silver atoms in DyAgGe are tetrahedrally surrounded by germanium atoms; two Ge1 at 271.7 pm and two Ge2 at 274.6 pm. Both of these distances compare well with the sum of the metallic radii for silver (144.5 pm [24]) and germanium (136.9 pm [24]) of 281.4 pm. The Ag–Ag distances of 306.8 pm within the trigonal prisms are significantly longer than in cubic close packed silver (288.9 pm [25]). These Ag–Ag contacts therefore do not significantly contribute to bonding. Considering that the rare earth atoms are by far the most electropositive component of the present compounds, they will largely have transferred their valence electrons to the silver–germanium polyanion. The compounds may therefore, to a first approximation, be described by the formula $Dy^{3+}[AgGe]^{3-}$. The [AgGe] polyanion as outlined in Fig. 3 is three-dimensional and forms large open tubes extending along the z-axis in which the dysprosium atoms are embedded.

3.2. Chemical properties

Powders and single crystals of the ternary LnAgGe germanides are light grey and stable in air for long periods of time. No decomposition whatsoever was observed after several months. Single crystals exhibit metallic lustre. They form long needles (up to 2 mm long). Powdered samples of the germanides are not visibly attacked by water or dilute hydrochloric acid. While they slowly dissolve in concentrated hydrochloric acid, immediate dissolution takes place in dilute nitric acid.

3.3. Magnetic susceptibilities

The temperature dependences of the inverse susceptibilities of GdAgGe, DyAgGe and ErAgGe are displayed in Fig. 4. Above 30 K the inverse susceptibilities show Curie–Weiss behaviour. The experimental magnetic moments obtained from the high temperature slopes of the $1/\chi$ vs. T plots according to $\mu_{exp} = 2.83[\chi(T-\theta)]^{1/2}\mu_B$ agree well with the theoretical effective moments μ_{eff} obtained from the relation $\mu_{eff} = g[(J(J+1)]^{1/2}\mu_B$ (see Table 2). The paramagnetic Curie temperatures θ (Weiss-constants) were ob-

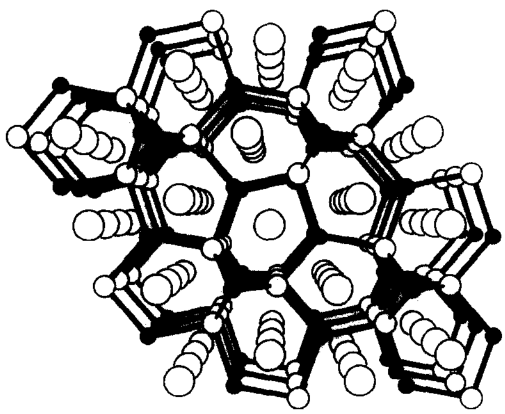

Fig. 3. Perspective view of the DyAgGe structure along the z-axis [26]. The dysprosium, silver and germanium atoms are shown as large open, medium open and small filled circles respectively. The three-dimensional [AgGe] polyanion is outlined.

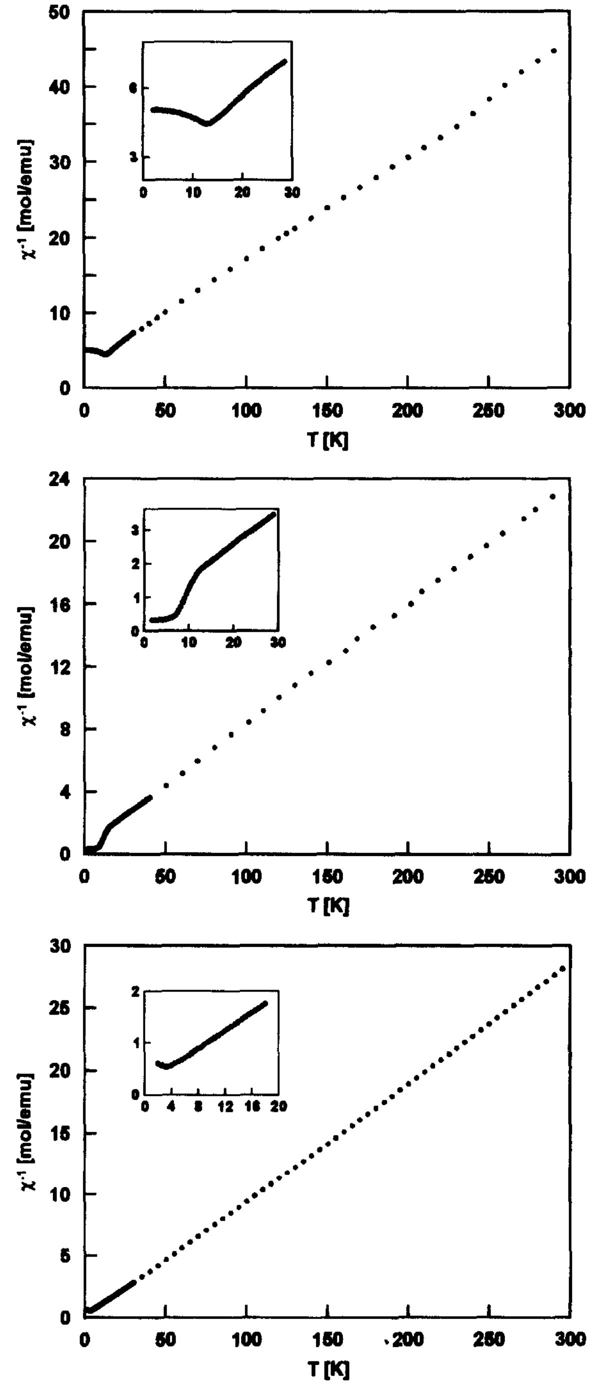

Fig. 4. Temperature dependence of the inverse magnetic susceptibility of GdAgGe, DyAgGe and ErAgGe measured at a magnetic flux density of 0.1 T.

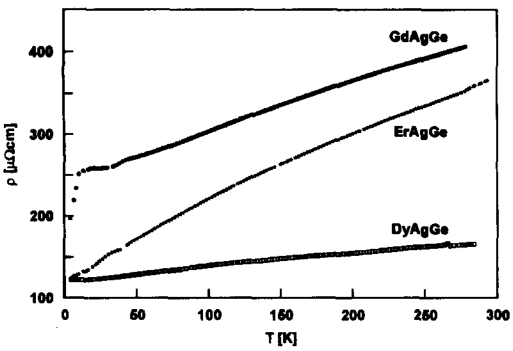

Fig. 5. Temperature dependence of the specific resistivity of GdAgGe, DyAgGe and ErAgGe.

tained by extrapolation of the linear $1/\chi$ vs. T plots to $1/\chi = 0$ (see Table 2). Antiferromagnetic ordering at 13.0(5) and 3.3(1) K for GdAgGe and ErAgGe respectively is observed at low temperatures. In contrast, a vanishing $1/\chi$ vs. T behaviour is observed for DyAgGe, indicating ferromagnetic ordering. The Curie temperature of 14.0(2) K was deduced from the inflection point of the magnetization versus temperature dependence measured at a magnetic flux density of 0.001 T. Our first magnetization versus field measurements indicated complex field-dependent, possibly multistep metamagnetic behaviour. More detailed investigations of this and the other LnAgGe compounds are currently in progress.

3.4. Electrical resistivity

The specific resistivities (see Fig. 5) of the three compounds decrease with decreasing temperature, as is usual for metallic conductors. The room temperature values amount to 400, 165 and 365 μΩcm for GdAgGe, DyAgGe and ErAgGe respectively, indicating quite good metallic conductivity. For comparison, gadolinium and silver have room temperature specific resistivity values of 140 and 1.6 μΩcm respectively [27]. Below about 15 K, the specific resistivity of GdAgGe decreases much more steeply, indicating a decrease in spin-disorder resistivity which results from the antiferromagnetic phase transition.

4. Conclusions

A series of rare earth metal–silver–germanides has been prepared, and the ordering between the silver and germanium atoms has been studied by X-ray diffraction on single crystals. All compounds adopt the ZrNiAl structure, a ternary ordered variant of the well known Fe_2P type. Investigations of the physical properties show metallic behaviour and antiferromagnetic ordering at $T_N = 13.0(5)$ and 3.3(1) K for GdAgGe and ErAgGe respectively. DyAgGe orders ferromagnetically at $T_C = 14.0(2)$ K. A more detailed study of the transport properties of these interesting materials will be reported in a forthcoming paper.

5. Supplementary material available

Listings of the observed and calculated structure factors are available, details may be obtained from Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany by quoting the depository numbers CSD-404602 (GdAgGe), CSD-404601 (DyAgGe) and CSD-404600 (ErAgGe), the names of the authors and the journal citation.

Acknowledgments

We are grateful to W. Röthenbach for taking the Guinier powder patterns, to E. Brücher for the susceptibility measurements, to N. Rollbühler for the electrical conductivity measurements, and to Dr. W. Gerhartz (Degussa) for a generous gift of silver wire. The Stiftung Stipendienfonds des Verbandes der Chemischen Industrie supported our research by a Liebig grant to R.P.

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