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Magnetic properties of solid solutions with AlB_2-type structure in *R*–Ag–Al–Ge systems (*R* = Ce, Pr, Nd)

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For the AlB_2-type solid solutions formed in the quaternary systems *R*–Ag–Al–Ge (*R* = Ce, Pr, Nd) magnetic measurements have been performed in the magnetic fields up to5 T and in the temperature range 1.72-400 K. It is shown that these compounds fit to a Curie-Weiss expression above 80 K. The magnetic characteristics of the compounds (ordering temperature, Curie-Weiss temperature, effective magnetic moment, high-field magnetic moment) have been determined. The effective paramagnetic moments are close to the values of free R^{3+} (*R* = Ce, Pr, Nd) ions.

Rare-earth / Silver / Aluminum / Germanium / Solid solution / X-ray diffraction / Magnetic measurements

Introduction

Rare-earth alloys are attracting interest because they form a number of magnetic materials. High electrical and thermal conductivity, and good corrosion resistance are arguments for silver and its alloys to be used; corrosion resistance and lightness are typical features of aluminum alloys. Germanides of rare-earth elements have high melting points, high-temperature strength, special electrical and mechanical properties.

Several crystal structure investigations of intermetallics formed in *R*–Ag–Ge and *R*–Al–Ge systems (where *R* is a light rare-earth metal) have been carried out [1-7], but information about the magnetic properties is scarce. In particular, among the 12 ternary compounds with AlB_2-type structure (Pearson code *hP*3, space group *P*6/*mmm*): $LaAg_{0.8}Ge_{1.2}$ (773 K), $CeAg_{0.8}Ge_{1.2}$ (773 K), $CeAg_{0.8\text{-}0.67}Ge_{1.2\text{-}1.33}$ (1123 K), $PrAg_{0.8}Ge_{1.2}$ (873 K), $NdAg_{0.7}Ge_{1.3}$ (1073 K), EuAgGe (673 K), $EuAg_{0.8}Ge_{1.2}$ (973 K), $GdAg_{0.6}Ge_{1.4}$ (873 K) [1-3] and $LaAl_{1.8\text{-}1.5}Ge_{0.2\text{-}0.5}$ (773 K), $CeAl_{1.6\text{-}1.5}Ge_{0.4\text{-}0.5}$ (773 K), $PrAl_{1.55\text{-}1.48}Ge_{0.45\text{-}0.52}$ (673 and 873 K), $NdAl_{1.63\text{-}1.50}Ge_{0.37\text{-}0.50}$ (1273 K), $SmAl_{1.5}Ge_{0.5}$ (1273 K), and $EuAl_{1.08\text{-}1.00}Ge_{0.92\text{-}1.00}$ (873 K) [4-7], the magnetic behavior has been studied only for two of them, namely, $CeAg_{0.67}Ge_{1.33}$ [8] and $CeAl_{1.5}Ge_{0.5}$ [9]. According to [8] the $CeAg_{0.67}Ge_{1.33}$ compound shows soft ferromagnetic properties with a Curie temperature of T_C = 7.5 K. The $CeAl_{1.5}Ge_{0.5}$ compound orders ferromagnetically below T_C = 6.15 K [9].

The existence in the quaternary systems *R*–Ag–Al–Ge (*R* = Ce, Pr, Nd) at 873 K of complete solid solutions based on the ternary germanides $CeAg_{0.8}Ge_{1.2}$–$CeAl_{1.6\text{-}1.5}Ge_{0.4\text{-}0.5}$, $PrAg_{0.8}Ge_{1.2}$–$PrAl_{1.55\text{-}1.48}Ge_{0.45\text{-}0.52}$, and $NdAg_{0.7}Ge_{1.3}$–$NdAl_{1.63\text{-}1.50}Ge_{0.37\text{-}0.50}$ with AlB_2-type structure, was reported in [10]. The aim of this work was to investigate the magnetic properties of the AlB_2-type solid solutions in the quaternary systems {Ce, Pr, Nd}–Ag–Al–Ge.

Experimental

17 four-component alloys with nominal compositions $R_{33.3}(Ag,Al,Ge)_{66.7}$ were prepared by direct melting of the constituent elements (Ce, Pr, Nd ≥ 99.83 wt.%, Al ≥ 99.985 wt.%, Ag and Ge ≥ 99.999 wt.%) in an arc-furnace under purified (Ti-gettered) argon atmosphere on a water-cooled copper hearth. The samples were annealed at 873 K in evacuated quartz ampoules for 1 month and subsequently quenched in cold water. The weight loss during the preparation of the samples was less than 1% of the total mass, which was 1 g for each alloy.

Phase analysis was carried out using X-ray powder diffraction data collected on a diffractometer DRON-2.0M (Fe *K*α radiation) in the angular range $20 \le 2\theta \le 100^\circ$. The profile and structural parameters were refined by the Rietveld method, using the program DBWS-9807 [11]. Magnetization and dc

magnetic susceptibility measurements were performed on a SQUID magnetometer (Quantum Design MPMS) in magnetic fields up to 5 T and in the temperature range 1.72-400 K.

Results and discussion

Structural (phases, their structure types, refined unit-cell parameters) and magnetic (type of spin order, ordering and Curie-Weiss temperatures T_{ord} and θ_p, effective magnetic moment μ_{eff} and magnetic moment $\sigma_{1.72K,5T}$ measured at T = 1.72 K in $\mu_0 H$ = 5 T) data for the samples of the *R*–Ag–Al–Ge systems (*R* = Ce, Pr, Nd) are listed in Tables 1-3. The temperature dependencies of the inverse magnetic susceptibility for the alloys at 0.1 T are shown it Figs. 1-3, where the solid line is a fit of the experimental data to the Curie-Weiss law. The insets display the field dependence of the magnetization at *T* = 1.72 K and its temperature dependence at 0.1 T.

Table 1 Structural and magnetic data for the $CeAg_{0.8}Ge_{1.2}$–$CeAl_{1.6\text{-}1.5}Ge_{0.4\text{-}0.5}$ solid solution.

Sample composition, at.%	Phase	Structure type	Unit-cell parameters			Spin order	T_{ord}, K	σ_s, μ_B	θ_p, K	μ_{eff}, μ_B
			a, nm	*c*, nm	*V*, nm3					
$Ce_{33.3}Ag_{23.3}Al_{6.7}Ge_{36.7}$	$CeAg_{0.70}Al_{0.20}Ge_{1.10}$ CeAgGe	AlB_2 LiGaGe	0.43901(6) 0.4506(1)	0.41407(8) 0.7834(8)	0.06911(2) 0.1377(2)	F	5.5	0.9	-13.2	2.59
$Ce_{33.3}Ag_{20.0}Al_{13.3}Ge_{33.4}$	$CeAg_{0.60}Al_{0.40}Ge_{1.00}$	AlB_2	0.43832(7)	0.41603(9)	0.06922(2)	F	5.7	1.2	12.2	2.58
$Ce_{33.3}Ag_{16.7}Al_{20.0}Ge_{30.0}$	$CeAg_{0.50}Al_{0.60}Ge_{0.90}$	AlB_2	0.43619(6)	0.42133(8)	0.06942(2)	F	3.3	0.7	-50.4	2.54
$Ce_{33.3}Ag_{13.3}Al_{26.7}Ge_{26.7}$	$CeAg_{0.40}Al_{0.80}Ge_{0.80}$	AlB_2	0.43487(6)	0.42474(7)	0.06956(2)	F	5.8	0.8	-17.3	2.50
$Ce_{33.3}Ag_{2.7}Al_{46.7}Ge_{17.3}$	$CeAg_{0.08}Al_{1.40}Ge_{0.52}$	AlB_2	0.43480(5)	0.42953(7)	0.07032(2)	F	5.4	0.8	-19.0	2.44

Table 2 Structural and magnetic data for the $PrAg_{0.8}Ge_{1.2}$–$PrAl_{1.55\text{–}1.48}Ge_{0.45\text{–}0.52}$ solid solution.

Sample composition, at.%	Phase	Structure type	Unit-cell parameters			Spin order	T_{ord}, K	σ_s, μ_B	θ_p, K	μ_{eff}, μ_B
			a, nm	*c*, nm	*V*, nm^3					
$Pr_{33.3}Ag_{23.3}Al_{6.7}Ge_{36.7}$	$PrAg_{0.70}Al_{0.20}Ge_{1.10}$	AlB_2	0.43722(6)	0.40981(7)	0.06785(2)	F	8.1	1.3	4.7	3.57
$Pr_{33.3}Ag_{16.7}Al_{16.7}Ge_{33.3}$	$PrAg_{0.50}Al_{0.50}Ge_{1.00}$	AlB_2	0.43415(6)	0.41652(8)	0.06799(2)	F	7.6	1.2	-0.6	3.65
$Pr_{33.3}Ag_{13.3}Al_{20.0}Ge_{33.4}$	$PrAg_{0.40}Al_{0.60}Ge_{1.00}$	AlB_2	0.43215(8)	0.41858(9)	0.06769(3)	F F	7.6 42.5	1.2	-7.2	3.63
$Pr_{33.3}Ag_{12.7}Al_{26.7}Ge_{27.3}$	$PrAg_{0.38}Al_{0.80}Ge_{0.82}$	AlB_2	0.43368(5)	0.41929(7)	0.06830(2)	F	7.6	1.4	2.9	3.62
$Pr_{33.3}Ag_{8.4}Al_{33.3}Ge_{25.0}$	$PrAg_{0.25}Al_{1.00}Ge_{0.75}$	AlB_2	0.43253(6)	0.42244(7)	0.06844(2)	F AF	3.2 54.8	1.3	-24.1	3.94
$Pr_{33.3}Ag_{3.3}Al_{43.4}Ge_{20.0}$	$PrAg_{0.10}Al_{1.30}Ge_{0.60}$	AlB_2	0.43288(9)	0.42389(9)	0.06880(2)	F	4.7	1.4	5.1	3.60

Table 3 Structural and magnetic data for the $NdAg_{0.7}Ge_{1.3}$–$NdAl_{1.63\text{–}1.50}Ge_{0.37\text{–}0.50}$ solid solution.

Sample composition, at.%	Phase	Structure type	Unit-cell parameters, nm			Spin order	T_{ord}, K	σ_s, μ_B	θ_p, K	μ_{eff}, μ_B
			a, nm	*c*, nm	*V*, nm^3					
$Nd_{33.3}Ag_{20.0}Al_{6.7}Ge_{40.0}$	$NdAg_{0.60}Al_{0.20}Ge_{1.20}$	AlB_2	0.43121(7)	0.41274(9)	0.06646(2)	F AF	4.9 10.5	1.9	0.7	3.68
$Nd_{33.3}Ag_{17.3}Al_{13.3}Ge_{36.0}$	$NdAg_{0.52}Al_{0.40}Ge_{1.08}$	AlB_2	0.43379(6)	0.41144(8)	0.06705(2)	F AF	5.0 13.7	1.8	5.2	3.64
$Nd_{33.3}Ag_{14.0}Al_{20.0}Ge_{32.7}$	$NdAg_{0.42}Al_{0.60}Ge_{0.98}$	AlB_2	0.43177(5)	0.41493(6)	0.06700(1)	F AF	5.1 11.9	1.8	5.3	3.60
$Nd_{33.3}Ag_{11.3}Al_{26.7}Ge_{28.7}$	$NdAg_{0.34}Al_{0.80}Ge_{0.86}$	AlB_2	0.43048(5)	0.41811(6)	0.06710(1)	F	9.9	1.7	5.3	3.73
$Nd_{33.3}Ag_{6.7}Al_{36.7}Ge_{23.3}$	$NdAg_{0.20}Al_{1.10}Ge_{0.70}$	AlB_2	0.43138(4)	0.41951(5)	0.06761(1)	AF	2.5	1.7	1.0	3.73
$Nd_{33.3}Ag_{2.7}Al_{46.7}Ge_{17.3}$	$NdAg_{0.08}Al_{1.40}Ge_{0.52}$	AlB_2	0.43138(5)	0.42100(6)	0.06785(1)	F F F	8.1 26.8 49.5	1.5	12.7	3.67

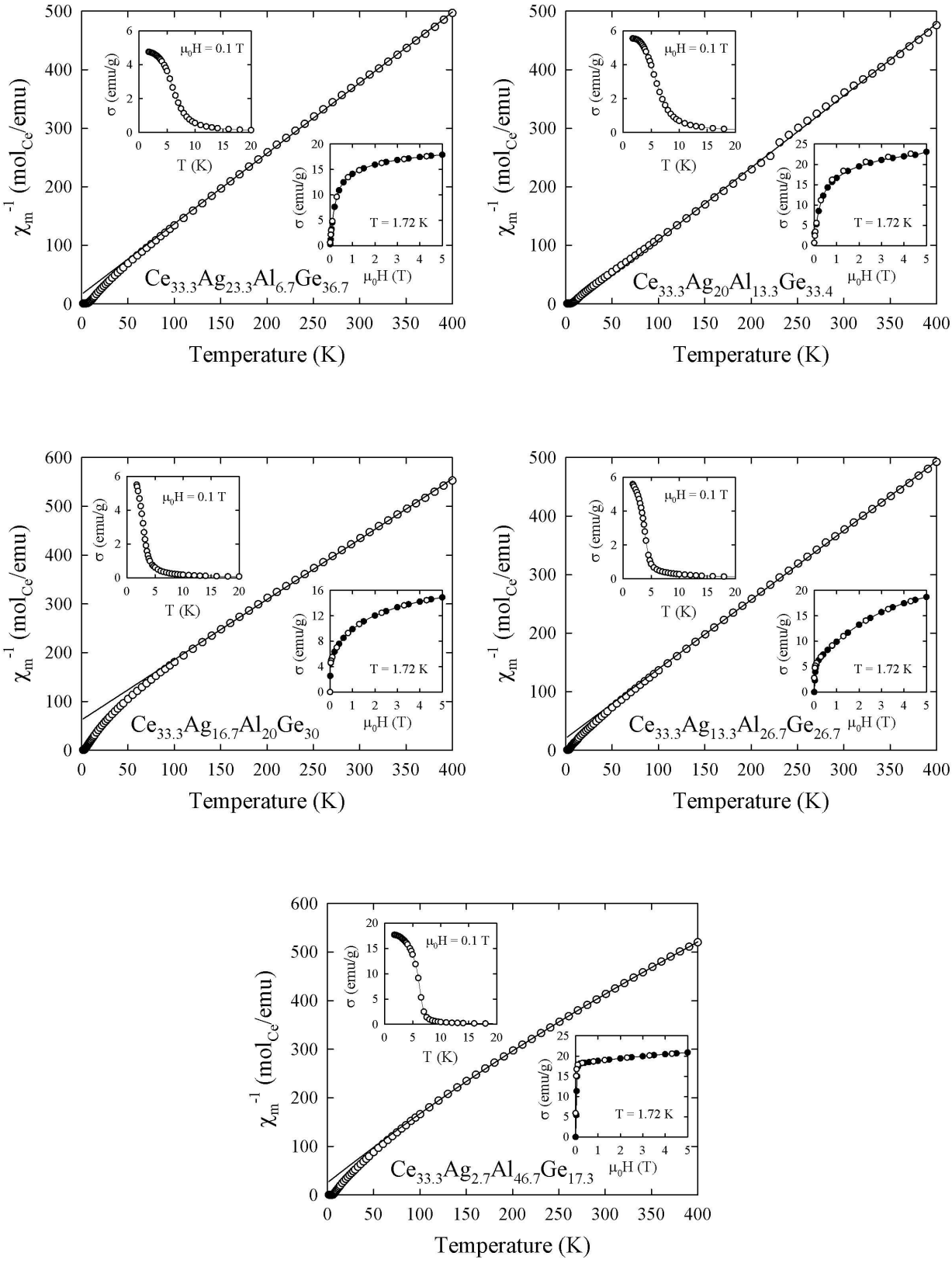

Fig. 1 Inverse magnetic susceptibility and magnetization as a function of temperature at 0.1 T and field dependence of the magnetization at T = 1.72 K for certain compositions of the solid solution $CeAg_{0.8}Ge_{1.2}$–$CeAl_{1.6\text{-}1.5}Ge_{0.4\text{-}0.5}$.

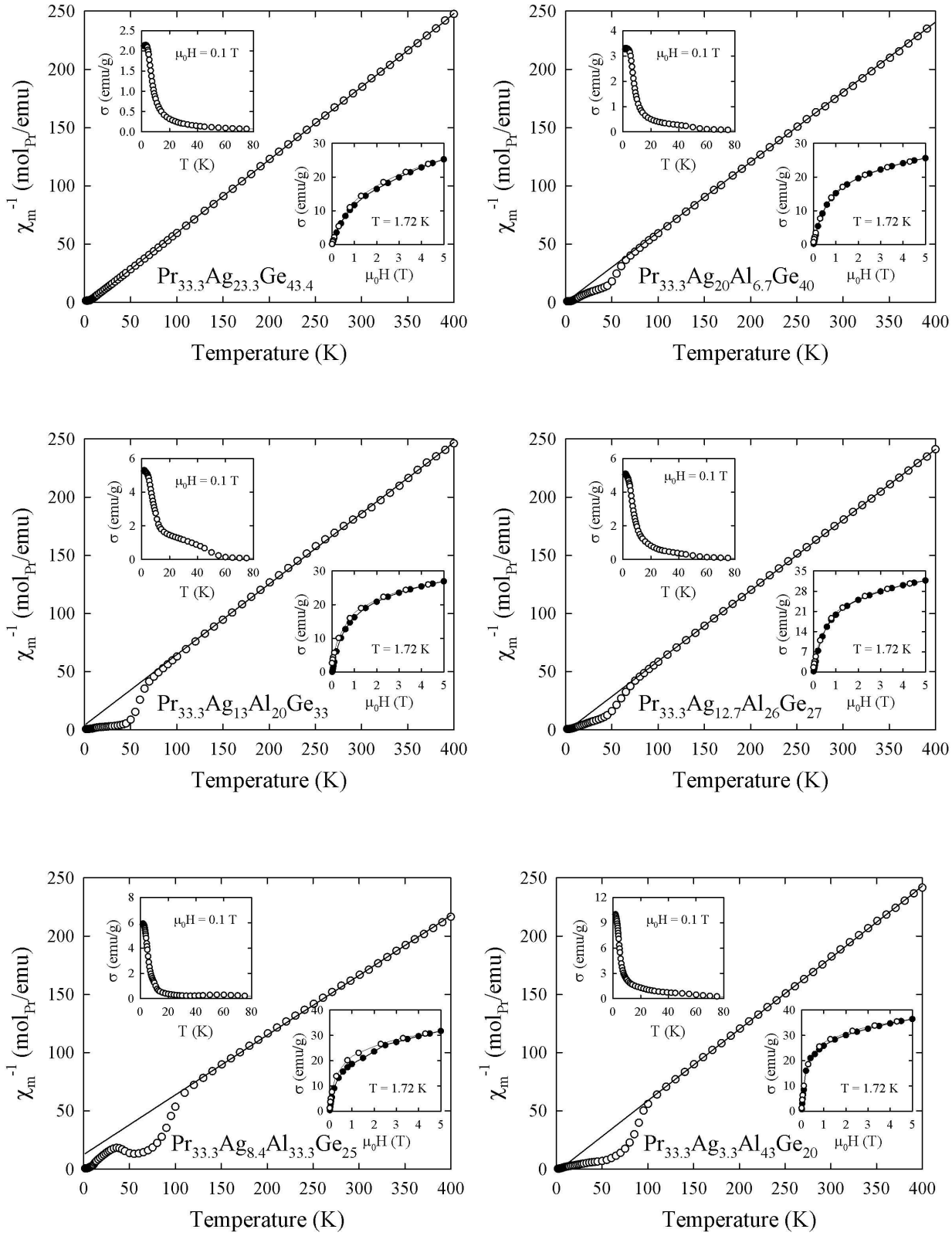

Fig. 2 Inverse magnetic susceptibility and magnetization as a function of temperature at 0.1 T and field dependence of the magnetization at T = 1.72 K for the certain compositions of the solid solutions $PrAg_{0.8}Ge_{1.2}$–$PrAl_{1.55\text{-}1.48}Ge_{0.45\text{-}0.52}$.

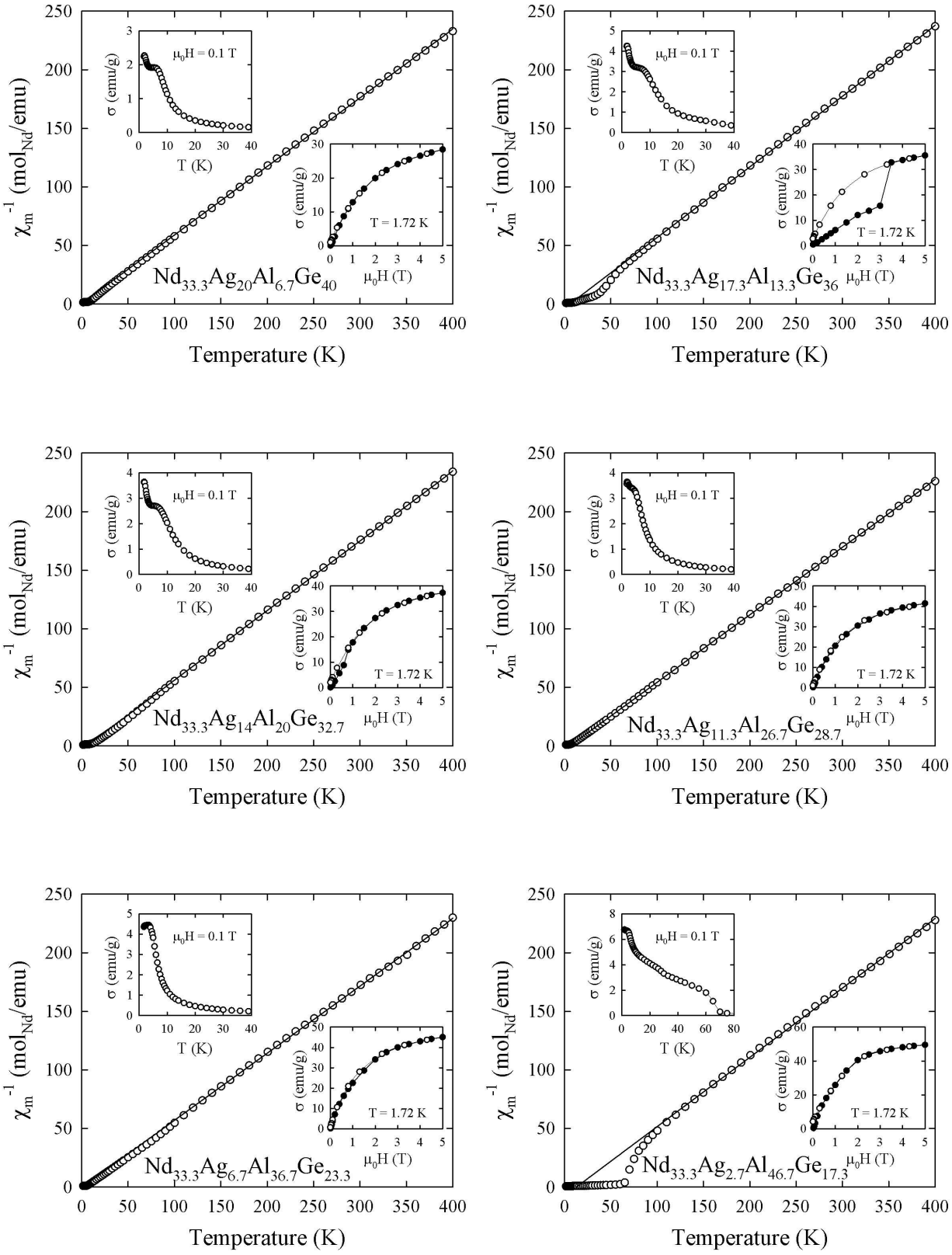

Fig. 3 Inverse magnetic susceptibility and magnetization as a function of temperature at 0.1 T and field dependence of the magnetization at T = 1.72 K for the certain compositions of the solid solutions $NdAg_{0.7}Ge_{1.3}$–$NdAl_{1.63\text{-}1.50}Ge_{0.37\text{-}0.50}$.

According to the X-ray powder diffraction patterns all of the synthesized alloys are single-phase samples (except $Ce_{33.3}Ag_{23.3}Al_{6.7}Ge_{36.7}$) and their crystal structures belong to the hexagonal AlB_2 type. Within the homogeneity ranges $CeAg_{0.8}Ge_{1.2}$–$CeAl_{1.6\text{-}1.5}Ge_{0.4\text{-}0.5}$, $PrAg_{0.8}Ge_{1.2}$–$PrAl_{1.55\text{-}1.48}Ge_{0.45\text{-}0.52}$, and $NdAg_{0.7}Ge_{1.3}$–$NdAl_{1.63\text{-}1.50}Ge_{0.37\text{-}0.50}$, the *a*-parameter decreases with increasing Al content (0-54.3 at.%) and decreasing Ag and Ge content (26.7-0 and 43.3-12.3 at.%, respectively), whereas the *c*-parameter increases. The replacement of Ag and Ge atoms (covalent radii r = 0.134 and 0.122 nm, respectively) by Al atoms (r = 0.118 nm) influences mainly the *a*-parameter, which reflects the contact distances between the small atoms in the structure $\left(\delta_{M-M} = a/\sqrt{3}\right)$. The variation of the unit-cell parameters within the homogeneity ranges of the AlB_2-type compounds in the quaternary systems {Ce, Pr, Nd}–Ag–Al–Ge is shown in Fig. 4.

The magnetic measurements show that the magnetic susceptibility of the AlB_2-type solid solutions follows the Curie-Weiss law

$$\chi_M = \frac{C_M}{T - \theta_p}$$

in the temperature range 20-400 K for $CeAg_{0.8}Ge_{1.2}$–$CeAl_{1.6\text{-}1.5}Ge_{0.4\text{-}0.5}$, 80-400 K for $PrAg_{0.8}Ge_{1.2}$–$PrAl_{1.55\text{-}1.48}Ge_{0.45\text{-}0.52}$ and 40-400 K for $NdAg_{0.7}Ge_{1.3}$–$NdAl_{1.63\text{-}1.50}Ge_{0.37\text{-}0.50}$. As a rule, at low temperatures fairly complex magnetic ordering with notable ferromagnetic component is observed for these compounds. For the solid solution $NdAg_{0.7}Ge_{1.3}$–$NdAl_{1.63\text{-}1.50}Ge_{0.37\text{-}0.50}$ the replacement of Ag and Ge by Al atoms leads to an increase of the ordering temperature T_C and a decrease of the moment $\sigma_{1.72K,5T}$. For the solid solution $PrAg_{0.8}Ge_{1.2}$–$PrAl_{1.55\text{-}1.48}Ge_{0.45\text{-}0.52}$ the replacement of Ag and Ge by Al atoms results in a decrease of T_{ord}, while $\sigma_{1.72K,5T}$ remains almost constant. For the investigated compositions of the solid solution $CeAg_{0.8}Ge_{1.2}$–$CeAl_{1.6\text{-}1.5}Ge_{0.4\text{-}0.5}$, T_{ord} is ~5.6 K and $\sigma_{1.72K,5T}$ decreases slightly when Ag and Ge atoms are replaced by Al atoms. The small hysteresis effect observed for the alloys indicates soft character of their magnetism. The measured effective paramagnetic moments per formula unit, calculated by the formula

$$\mu_{eff} = 2.828\sqrt{\chi_M \cdot (T_i - \theta_p)},$$

are close to the values of free R^{3+} ions (the theoretical effective paramagnetic moments are 2.54 for Ce^{3+}, 3.58 for Pr^{3+}, and 3.62 for Nd^{3+}).

Conclusions

An investigation of the magnetic properties of the solid solutions $CeAg_{0.8}Ge_{1.2}$–$CeAl_{1.6\text{-}1.5}Ge_{0.4\text{-}0.5}$, $PrAg_{0.8}Ge_{1.2}$ – $PrAl_{1.55\text{-}1.48}Ge_{0.45\text{-}0.52}$, and $NdAg_{0.7}Ge_{1.3}$–$NdAl_{1.63\text{-}1.50}Ge_{0.37\text{-}0.50}$ with AlB_2-type structure has been carried out. The results of the dc magnetic susceptibility measurements revealed the Curie-Weiss paramagnetic behavior. The effective paramagnetic moments of the compounds measured above 80 K are close to the respective values of the free R^{3+} (*R* = Ce, Pr, Nd) ions, which is an evidence of the trivalent state of the rare-earth atoms. These results indicate that only the rare-earth atoms carry magnetic moments. At low temperatures, all the compounds studied order magnetically. The observed fairly complex behaviors of the magnetization as a function of temperature and magnetic field strength hint at complicated magnetic structures and multiple phase transitions occurring in most of these materials.

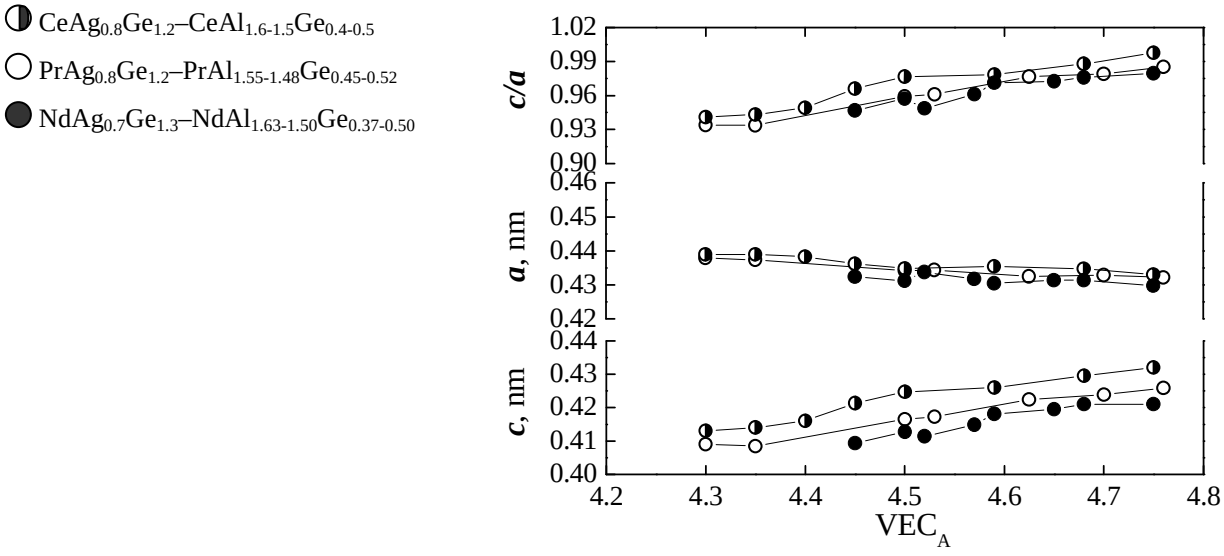

Fig. 4 Unit-cell parameters within the homogeneity ranges of the AlB_2-type compounds in the quaternary systems {Ce,Pr,Nd}–Ag–Al–Ge as a function of the valence electron concentration VEC_A.

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