Structure, Magnetic, and Electrical Properties of the *Ln*Ag$_6$In$_6$ Intermetallics (*Ln* = La, Ce, Pr, and Nd)

V. I. Zaremba,* Ya. M. Kalychak,* Ya. V. Galadzhun,* W. Suski,†·‡·[1] and K. Wochowski†

*Department of Inorganic Chemistry, Lviv State University, 290005 Lviv, Ukraine; †Polish Academy of Sciences,
W. Trzebiatowski Institute of Low Temperature and Structure Research, P.O. Box 1410, 50-950 Wrocław 2, Poland; and
‡International Laboratory of High Magnetic Fields and Low Temperatures, ul. Gajowicka 95, 53-421 Wrocław, Poland

Tetragonal *Ln*Ag$_6$In$_6$ compounds have been obtained for the first time for *Ln* = La, Pr, and Nd. CeAg$_{6.4}$In$_{5.6}$ has slightly different stoichiometry, and a Pr compound also exists with this composition. These materials exhibit ThMn$_{12}$ type structure (*I4/mmm*). LaAg$_6$In$_6$ is diamagnetic whereas other compounds are paramagnetic following the Curie–Weiss law above 100 K. For paramagnetic compounds the effective magnetic moments are fairly close to free ion values and Weiss constants are very small. NdAg$_6$In$_6$ exhibits in the $\chi(T)$ plot a maximum at 5 K which most probably corresponds to the Néel point. At 1.7 K the magnetization of the paramagnetic samples linearly depends on magnetic field strength up to 5 T. The temperature dependence of the electrical resistvity, $\rho(T)$, suggests a metallic character of all compounds without any indication of superconducting transition. The electrical resistivity of PrAg$_{6.4}$In$_{5.6}$ is slightly higher than that for PrAg$_6$In$_6$ and it is most probably related to some disorder in an occupation of the crystallographic positions. © 1999 Academic Press

Key Words: crystal structure; magnetic properties; electrical properties; lanthanide intermetallics.

INTRODUCTION

The tetragonal, ThMn$_{12}$-type compounds of the *f*-electron elements, usually existing as ternaries, have caused recently a broad interest (for references see (1)). Those compounds containing Fe in higher concentration seem to be promising magnetic materials (see (1)). The compounds containing Cu have been reported to show the heavy fermion (HF) state (2, 3) and, e.g., the UCu$_{4+x}$Al$_{8-x}$ system depending on *x* can exhibit the Landau–heavy-fermion-liquid versus non-Fermi-liquid behavior (3). However, CeAg$_4$Al$_8$ does not exhibit superconductivity, magnetic order, or the HF state down to the lowest temperature (2). These potentially HF materials contain Al as the third, stabilizing component.

Recently, we reported on magnetic and related properties of the lanthanide compounds containing In instead of Al; however, this preliminary research has not revealed HF behavior (4, 5). However, an indication of magnetic order setup at low temperature has been obtained for *Ln* = Gd, Tb, and Dy.

Now we are reporting on magnetic structure and related properties of *Ln*Ag$_6$In$_6$ compounds with *Ln* = La, Pr, and Nd and *Ln*Ag$_{6.4}$In$_{5.6}$ with *Ln* = Ce and Pr. It should be noted that EuAg$_4$In$_8$ represents its own structure type with space group *P6/mmm* (6).

EXPERIMENTAL DETAILS

Ln–Ag–In alloys have been prepared by melting the elements in stoichiometric quantities in an arc furnace under a protective argon atmosphere. This procedure has been followed by prolonged annealing at about 670 K for 2 weeks. The magnetic susceptibility and electrical resistivity measurements have been performed on a bulk piece of polycrystalline material.

The magnetic susceptibility has been investigated in the temperature range 1.7–300 K using a SQUID magnetometer technique in a magnetic field of 0.5 *T*. The magnetization has been measured at $T = 1.7$ K in magnetic fields up to 5 *T*. Electrical resistivity has been investigated in the temperature range $T = 4.2$–300 K.
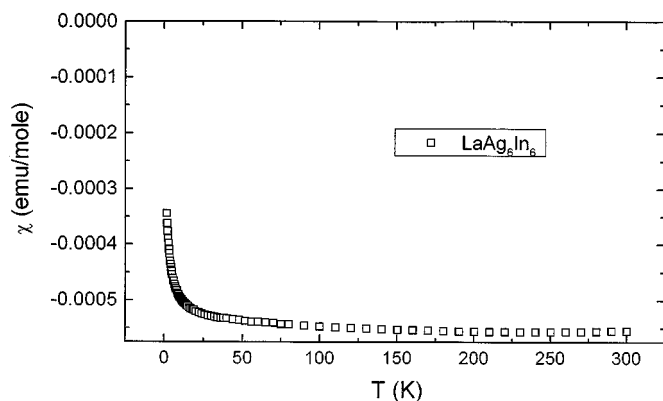
RESULTS AND DISCUSSION

We have succeeded in obtaining *Ln*Ag$_{\sim6}$In$_{\sim6}$ -type compounds for light lanthanides only, namely for La–Nd, and we do not know the reason why these compounds are not formed for other lanthanides. As mentioned before, EuAg$_4$In$_8$ exhibits different crystal structure and different stoichiometry (6). The exact 1 : 6 : 6 stoichiometry is preserved for *Ln* = La, Pr, and Nd. The existence of CeAg$_{6.4}$In$_{5.6}$ can only result from the possibility of the mixed valence
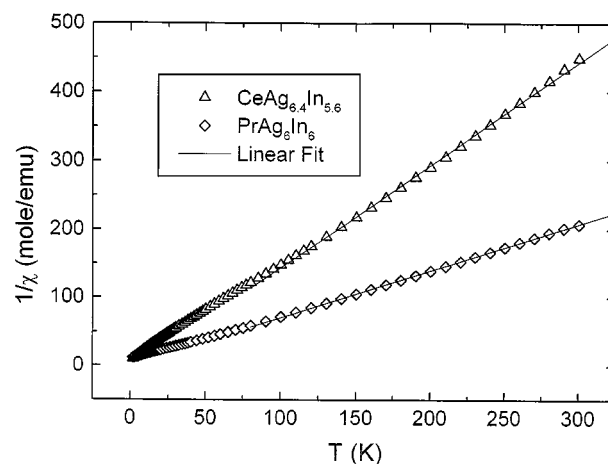

TABLE 1
Structural and Magnetic Data

Ln	a (nm)	c (nm)	p_{eff} (μ_B)	θ (K)	T_N (K)
		a. *Ln*Ag$_6$In$_6$			
La	0.9676(4)	0.5745(3)			
Pr	0.9669(3)	0.5708(3)	3.41	−2.83	
Nd	0.9650(2)	0.5722(2)	3.43	−2.15	5
		b. LnAg$_{6.4}$In$_{5.6}$			
Ce	0.9711(3)	0.5693(2)	2.32	3.84	
Pr	0.9678(2)	0.5701(4)			

FIG. 2. Reciprocal magnetic susceptibility of CeAg$_{6.4}$In$_{5.6}$ (triangles) and PrAg$_6$In$_6$ (diamonds) versus temperature, $T = 1.7$–300 K, measured in magnetic field of 0.5 T. Solid line is a fit to the Curie–Weiss law.

state of Ce (Ce^{3+} and Ce^{4+}); however, this hypothesis needs further studies. At present, we do not understand why these compounds exist in the 1 : 6 : 6 stoichiometry only, except for the Pr alloy which has also a PrAg$_{6.4}$In$_{5.6}$ form. In turn, *Ln*Cu$_{\sim 5}$In$_{\sim 7}$ compounds have only that stoichiometry (4), whereas the *Ln*Cu$_x$Al$_{12-x}$ alloys are known for $4 \leq x \leq 6$ (1). The lattice parameters of the investigated compounds are collected in Table 1. They do not show any systematic trend for the various lanthanides, even though it is difficult to detect the lanthanide contraction. The ThMn$_{12}$-type structure provides three crystallographic positions for occupation by In and Ag but without a single crystal available one cannot decide about the distribution of these atoms in crystal lattice.

The results of magnetic measurements are collected in Table 1 and in Figs. 1–4. The magnetic susceptibility χ versus temperature of LaAg$_6$In$_6$ is shown in Fig. 1. It is seen that χ is diamagnetic in the whole investigated temperature range and very weakly temperature dependent. At low temperature an increase of χ is observed, which most probably results from paramagnetic impurities which are impossible to detect in the X-ray examination. The temperature dependence of the inverse magnetic susceptibility, $1/\chi$, for

CeAg$_{6.4}$In$_{5.6}$ and PrAg$_6$In$_6$ is presented in Fig. 2. The results for PrAg$_{6.4}$In$_{5.6}$ are very close to that for PrAg$_6$In$_6$ and, therefore, for the sake of clearance, they are plotted. One can see that the $\chi(T)$ follows the Curie–Weiss law above about 100 K (solid lines in Fig. 2) with the Weiss constants, $\theta = 3.84$ and -2.83 K, and with effective magnetic moments amounting to $p_{eff} = 2.32$ and 3.41 μ_B for CeAg$_{6.4}$In$_{5.6}$ and PrAg$_6$In$_6$, respectively. The values of p_{eff} are fairly close to free ion values and the deviation from the Curie–Weiss law at low temperature seems to result from a weak crystal field interaction. A metallic character (see electrical properties) of the investigated compounds should manifest itself in the Pauli paramagnetism contribution to the total magnetic susceptibility. However, the

FIG. 1. Magnetic susceptibility of LaAg$_6$In$_6$ versus temperature, $T = 1.7$–300 K, measured in magnetic field of 0.5 T.
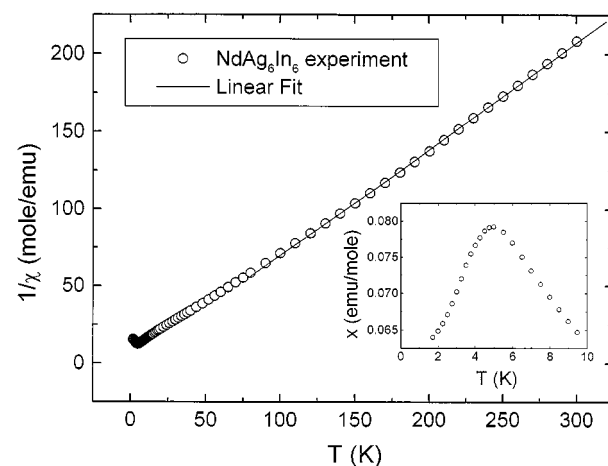
FIG. 3. Reciprocal magnetic susceptibility of NdAg$_6$In$_6$ versus temperature, $T = 1.7$–300 K, measured in magnetic field of 0.5 T. Solid line is a fit to the Curie–Weiss law. Inset shows the magnetic susceptibility versus temperature at low $T < 10$ K.
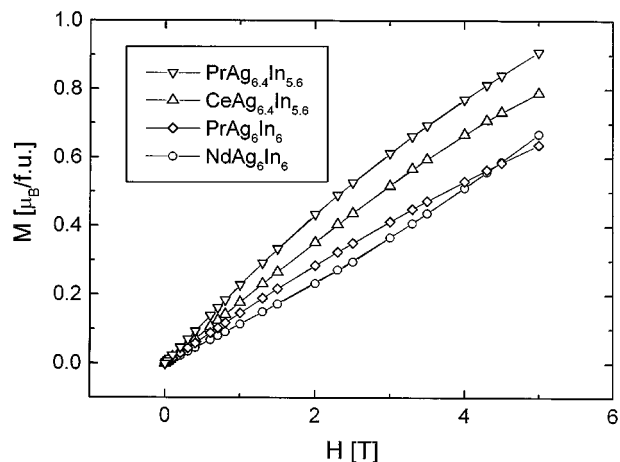
FIG. 4. Magnetization of $CeAg_{6.4}In_{5.6}$, $PrAg_6In_6$, $PrAg_{6.4}In_{5.6}$, and $NdAg_6In_6$ at $T = 1.7$ K versus magnetic field up to 5 T.

temperature range of our measurements is not high enough to observe this contribution. The inverse magnetic susceptibility of $NdAg_6In_6$ versus temperature is presented in Fig. 3. In principle, the same features as observed for the Nd compound have been detected for the Ce and Pr compounds: namely, the Curie–Weiss behavior of the $\chi(T)$ above about 50 K, the effective magnetic moment fairly close to the free ion value, $p_{eff} = 3.43\ \mu_B$, and the small negative Weiss constant, $\theta = -2.15$ K. However, at low temperature there is a maximum in the $\chi(T)$ plot, corresponding most probably to the Néel point, $T = 5$ K (see inset to Fig. 3). This conclusion is confirmed by recent low temperature heat capacity examination (7). It is clear that in the investigated paramagnetic compounds the exchange interactions (of the RKKY-type) are weak corresponding to the weak values of the Weiss constants and the CEF interactions are also weak in agreement with the small deviation of the effective magnetic moments from the free ion values. Hence, the observed magnetic order results from a delicate balance between both of these interactions. For the Nd compound, Nd^{3+} is a Kramers ion and the CEF ground state can be a magnetic doublet. For the Pr compound, the CEF ground state could be nonmagnetic level preventing any magnetic order. In turn, some valence instability in the Ce compound can also prevent the setup of magnetic order. These considerations are only working hypotheses and need further examination.

At $T = 1.7$ K, the negative magnetization of $LaAg_6In_6$ (not shown) decreases linearly with magnetic field (increase of the absolute values). Contrarily, the magnetization of the paramagnetic compounds almost linearly depends on the magnetic field strength (Fig. 4) in different ways: for the Ce and Pr compounds there is a trend for saturation but for the Nd compound the increase of the magnetization is faster than the linear for fields larger that $2T$. The difference in the

character of the magnetization versus field dependence for the Pr and the Nd compounds is probably related to the different CEF scheme in both compounds.

Preliminary electrical measurements have been carried out on the polycrystalline samples. They are presented in Figs. 5 and 6. Electrical resistivity exhibits a typical metallic character. In Fig. 5 the electrical resistivity for all samples is presented versus temperature in the range 4.2–300 K. It is seen that the residual resistivity of $LnAg_{6.4}In_{5.6}$ compounds is clearly higher (almost twice) than that for 1:6:6 materials. One possible reason for this behavior should be the existence of a more random atom distribution in the three possible eightfold positions. In Fig. 6 the electrical resistivity versus temperature at $T = 4.2–28$ K is shown for all materials. For the Nd compound the $\rho(T)$ plot does not provide any suggestion of magnetic ordering.

CONCLUSIONS

We have synthesized new $LnAg_6In_6$-type intermetallics ($Ln =$ La, Pr, and Nd) and additionally the parent $CeAg_{6.4}In_{5.6}$ and $PrAg_{6.4}In_{5.6}$ compounds, all exhibiting the $ThMn_{12}$-type structure (space group $I4/mmm$). The La compound is diamagnetic, whereas other compounds are paramagnetic. The Curie–Weiss law fits well to the data above 100 K with values of the effective magnetic moment fairly close to the free ion value and the small Weiss constant. At low temperature $NdAg_6In_6$ shows a maximum in
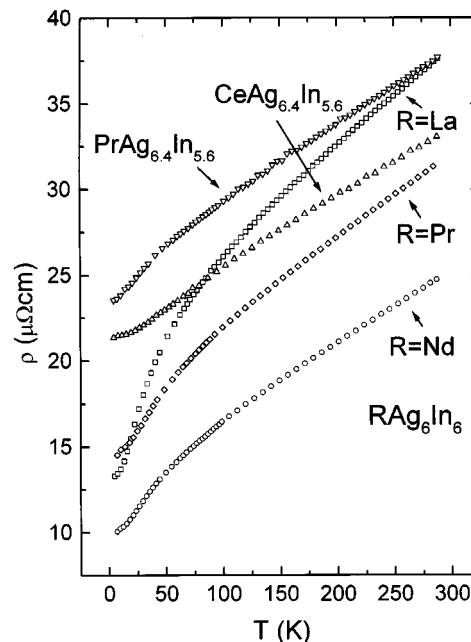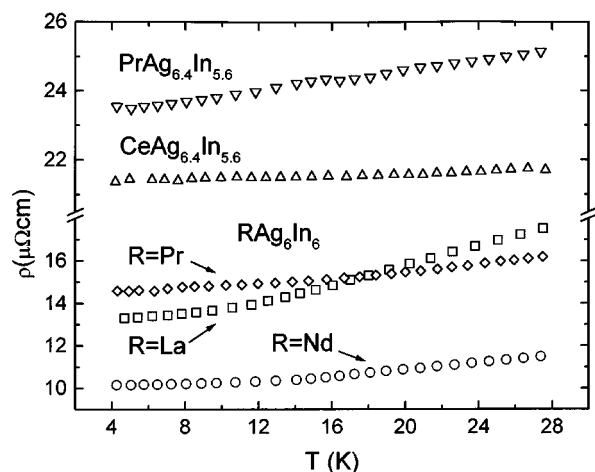

FIG. 5. Electrical resistivity of $LnAg_6In_6$, with $Ln =$ La, Pr, and Nd, and of $LnAg_{6.4}In_{5.6}$, with $Ln =$ Ce and Pr versus temperature, $T = 4.2–300$ K.

FIG. 6. Electrical resistivity of $LnAg_6In_6$, with Ln = La, Pr, and Nd, and of $LnAg_{6.4}In_{5.6}$, with Ln = Ce and Pr versus temperature, T = 4.2–28 K.

the $\chi(T)$ plot which probably corresponds to antiferromagnetic ordering with $T_N = 5$ K. The electrical resistivity of all compounds has metallic character; however, no confirmation of some magnetic instability was found for the Nd compound.

Precise crystal structure determinations are needed, first, to determine the mode of distribution of Ag and In atoms in the 8(f), 8(i), and 8(j) crystallographic positions. This is of a prime importance in order to understand both the conditions of stability of these new compounds and the magnetic

properties of the series. This could be achieved either from neutron powder diffraction or from precise X-ray single crystal analysis. Second, by using single crystals, one can undertake an accurate determination of the temperature dependence of electrical resistivity in various crystallographic directions to propose a mechanism governing the transport properties of these materials.

ACKNOWLEDGMENT

REFERENCES

1. W. Suski, *in* "Handbook on the Physics and Chemistry of Rare Earths" (K. A. Gschneidner Jr. and L. Eyring, Eds.), Vol. 22, Chap. 149, p. 143. Elsevier, Amsterdam, 1996.
2. U. Rauchschwalbe, U. Gottwick, U. Ahlheim, H. M. Meyer, and F. Steglich, *J. Less-Common Met.* **111,** 265 (1985).
3. T. Nishioka, Y. Kurakashi, R. Fukuda, and M. Kotani, *Czech. J. Phys.* **46,** 2065 (1996).
4. W. Suski, K. Wochowski, O. I. Bodak, Ya. M. Kalychak, V. I. Zaremba, and T. Mydlarz, *J. Alloys Comp.* **250,** 642 (1997).
5. W. Suski, H. Drulis, K. Wochowski, K. Tomala, R. Kmiec, Ya. M. Kalychak, V. I. Zaremba, T. Mydlarz, and A. Gilewski, *Z. Phys. B* **102,** 15 (1997).
6. L. V. Sysa, Ya. M. Kalychak, I. N. Steć, and Ya. V. Galadzhun, *Kristallografia* **39,** 821 (1994).
7. A. Czopnik, private communication.