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Ternary Compounds REAgSb$_2$, RE = Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm: Magnetism and Crystal Structure

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Ternary compounds REAgSb$_2$, RE = Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, have been synthesized by arc melting followed by a heat treatment at 600 or 800°C for 300 hr. The novel phases were all found to be isotypic with the structure type of ZrCuSi$_2$. Precise atom parameters have been derived for CeAgSb$_2$ from X-ray single crystal counter data: space group $P4/nmm$, a = 0.43641(9) nm, c = 1.0722(4) nm, and Z = 2. For 274 reflections ($|F_o| > 3\sigma$) the residual values are $R_F = \Sigma|\Delta F|/\Sigma|F_o| = 0.024$ and $R_w = 0.028$. A standardized set of atom parameters is provided. Magnetism of the REAgSb$_2$ phases in the temperature range 2.5 to 300 K is characterized by tripositive paramagnetic behavior of the rare-earth atoms. REAgSb$_2$ with RE = Y, La are weakly temperature-dependent paramagnets. In contrast, REAgSb$_2$ compounds with RE = Pr, Nd, Sm, Gd, Dy, Ho, Er, Tm are weak antiferromagnets with ordering temperatures lower than $T_N \sim 13$ K, and CeAgSb$_2$ is a noncolinear antiferromagnet ($T_M \sim 12$ K) with a remanent magnetization $\mu = 0.15\ \mu_B$ per Ce atom.

1. INTRODUCTION

The continued search for strongly correlated electron systems has prompted us toward a systematic investigation of (a) the constitution of the ternary systems: rare earth (cerium)–transition metal–pnicogen, (b) the formation of novel ternary compounds, (c) their crystal structures, and consequently, (d) the investigation of their structure-dependent physical (magnetic) properties.

Recently we reported on the structure and magnetism of ternary rare earth compounds RE(Fe, Co, Ni, Cu, Pd, Au)Sb$_2$ with the ZrCuSi$_2$ type (1, 2). In this paper we studied the crystal structure and the magnetic behavior of the REAgSb$_2$ series of ternary compounds.

2. EXPERIMENTAL

The alloys, each with a total weight of 1 g, were synthesized by argon arc melting from ingots of the elements starting from a nominal composition (at.%) 25RE–25Ag–50Sb. The materials used were commercially available as high purity elements: rare earths were in the form of ingots (99.9% pure, Auer-Remy GmbH., Germany); Ag powder was from Ögussa, Austria with a claimed purity of 99.9%; Sb was obtained as a rod (99.9% pure) from Johnson–Matthey & Co., United Kingdom.

To ensure homogeneity, the samples were remelted several times under an electric current which was as low as possible to minimize weight losses by vaporization of Sb, which were compensated for beforehand by including extra amounts of Sb. For heat treatment, the alloy buttons were sealed in evacuated quartz tubes and annealed for 14 days at 600 or 800°C. After heat treatment the alloys were quenched by submerging the silica tubes in water.

For further details of the sample preparation, the X-ray powder techniques employed for structural characterization, as well as of the equipment and type of magnetic measurements performed, the reader is referred to our recent publications on related series of compounds (1, 2). It shall be mentioned, however, that particularly the alloys with the light rare-earth elements La to Sm gave slightly diffuse X-ray patterns and therefore a stress-annealing step for 1 hr at 600°C under vacuum was employed on the powderized material prior to the X-ray experiments.

3. RESULTS AND DISCUSSION

3.1. The Crystal Structure of CeAgSb$_2$

A rather small elongated single-crystal fragment was obtained by mechanical fragmentation of the well-crystallized solidified regulus of an alloy with the nominal composition (at.%) 25Ce–25Ag–50Sb which has been annealed for 2 weeks at 600°C in an evacuated quartz capsule.

X-ray intensity data were collected on an automatic four-circle diffractometer. Details of the experimental X-ray intensity data collection are summarized in Table 1. The only observed systematic extinctions were those of the n-glide plane, ($hk0$) for $h + k = 2n + 1$, compatible with $P4/nmm$ as the centrosymmetric space group with

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TABLE 1
Parameters for the $CeAgSb_2$ Single Crystal X-Ray Data Collection

Diffractometer type	Stoe–Nicolet
Wave length	Mo$K\alpha$, λ = 0.07107 nm
Crystal characteristics	15 × 25 × 40 μm
Temperature of measurement	T = 293 K
$\sin \vartheta_{max}/\lambda$	13.0 nm^{-1}
Reciprocal space	$\pm h$, $\pm k$, l
Criterion for unobserved reflections	$I_0 > 3\sigma(I_0)$
Number of unique reflections	292 ($274 I_0 > 3\sigma(I_0)$)
Criterion for unobserved reflections	$I_0 > 3\sigma(I_0)$
Extinctions observed	P-tetragonal, ($hk0$) for $h + k = 2n + 1$
Number of refined parameters	13
Scan mode	$\omega/2\vartheta$ scan
Mode of absorption correction	empirical, ψ-scans (4)
Linear absorption coefficient, μ	μ(Mo$K\alpha$) = 28.35 mm^{-1}
Structure solution program	SHELX-76

the highest symmetry. Since the lattice parameters and X-ray powder intensities of the novel REAgSb$_2$ phases revealed striking similarities to those of homologous NdFeSb$_2$ (1), a first structure model was assigned for Ce, Ag, and Sb atoms in the crystallographic positions of the ZrCuSi$_2$ type (3, 4). This structure model was satisfactorily refined using the SHELX-76 program system (5). The weights used were $w_i = 3.310/[\sigma^2(F) + 10^{-3}F^2]$ and structure factors with different weighting schemes had no significant influence on the atom parameters obtained. Refinement of the Ag and Sb occupancies revealed no significant deviation from full occupation. The final R values calculated for the anisotropic thermal parameters and secondary extinction were $R_F = 0.024$ and $R_w = 0.028$. At this stage a final electron density map was featureless, confirming the composition CeAgSb$_2$. Positional and thermal parameters are listed in Table 2 including interatomic distances up to 0.4 nm. A listing of F_o and F_c data is available on request.

3.2. Isotypic Compounds $REAgSb_2$

Room temperature X-ray patterns of samples of REAgSb$_2$, RE = Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, and Tm, which had been annealed at 600 or 800°C for 14 days revealed a convincing resemblance to the pattern of homologous CeAgSb$_2$ and were all completely indexed on the basis of a tetragonal unit cell (see Table 3). Employing the atom parameters derived for CeAgSb$_2$ (Table 2), excellent agreement is obtained between the experimentally observed and calculated X-ray powder intensities, confirming the isotypy with the crystal structure of ZrCuSi$_2$. The homogeneity and X-ray intensities further indicate only small transition metal deficiencies in correspondence with the nominal composition of the alloys (see Table 3).

The formation and stability of the REAgSb$_2$ series of compounds seems to be reduced with decreasing radius of the rare earth element and TmAgSb$_2$ is the smallest end member observed. No REAgSb$_2$ phase was found with the small rare earth metals Yb and Lu. After being annealed at 600°C these alloys instead were found to re-

TABLE 2
Crystallographic Data for CeAgSb$_2$

Atom	Site	x	y	z	Occupation	U_{11} (nm^2)	U_{33} (nm^2)
Sb1	2a	¾	¼	0	1.0	1.46(3)	1.20(4)
Ag	2b	¾	¼	½	0.99(1)	1.79(3)	1.49(5)
Ce	2c	¼	¼	0.23788(4)	1.0	1.18(2)	1.17(3)
Sb2	2c	¼	¼	0.67363(5)	1.0	1.22(2)	1.60(5)

Interatomic distances in CeAgSb$_2$[a]

Ce–4Sb2	0.3228	Ag–4Sb2	0.2868	Sb1–4Sb1	0.3085	Sb2–4Ag	0.2868
Ce–4Sb1	0.3356	Ag–4Ag	0.3085	Sb1–4Ce	0.3356	Sb2–4Ce	0.3228
Ce–4Ag	0.3558	Ag–4Ce	0.3558	Sb1–4Sb2	0.4123	Sb2–4Sb1	0.4123
Ce–4Ce	0.4364					Sb2–4Sb2	0.4364

Note. Space group $P4/nmm$-D_{4h}^7, No. 129, Z = 2; origin at center. a = 0.43641(9) nm, c = 1.0722(4) nm, c/a = 2.4569, V = 0.2042(1) nm^3, ρ = 7.99 Mg m^{-3}. Anisotropic thermal factors are expressed as $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*] \times 10^{-2}$; by symmetry $U_{11} = U_{22}$ and $U_{12} = U_{13} = U_{23} = 0$. Standard deviations are given in parentheses. The isotropic extinction parameter (SHELX-76) was 0.0025. The weighting scheme (SHELX-76) employed was $w(F) = 3.3097/[\sigma^2(F) + 10^{-3}F^2]$. Residual values R_F = 0.024, R_w = 0.028.

[a] Standard deviations generally are less than 10^{-4} nm.

TABLE 3
Crystallographic and Magnetic Data of Ternary Compounds *RE*AgSb$_2$

Compound	Heat treatment (°C)	Lattice parameters (nm)		c/a	V (nm^3)	T_N (K)	Θ_p (K)	μ_{eff} (μ_B)
		a	c					
YAgSb$_2$	800	0.42745(6)	1.0492(3)	2.4544	0.1917(1)	$\chi_0 = 0.7 \times 10^{-6}$ cm^3 g^{-1}		
LaAgSb$_2$	600	0.43898(7)	1.0842(3)	2.4699	0.2089(1)	$\chi_0 = 0.6 \times 10^{-6}$ cm^3 g^{-1}		
CeAgSb$_2$	600	0.43641(9)	1.0722(4)	2.4569	0.2042(1)	12.0[a]	−6	2.57
PrAgSb$_2$	600	0.43506(2)	1.0679(4)	2.4548	0.2021(2)	4.3	−2	3.61
NdAgSb$_2$	600	0.43357(7)	1.0624(3)	2.4505	0.1997(1)	4.4	−9	3.91
SmAgSb$_2$	600	0.43126(7)	1.0548(5)	2.4459	0.1961(1)	10.0	−41	0.8[b]
GdAgSb$_2$	600	0.42965(9)	1.0518(6)	2.4480	0.1941(1)	14.0	−35	7.8
GdAg$_{0.8}$Sb$_2$[d]	600	0.42956(8)	1.0514(3)	2.4478	0.1940(1)			
TbAgSb$_2$	600	0.42774(7)	1.0477(7)	2.4495	0.1917(2)	13.0	−14	9.6
TbAgSb$_2$	800	0.42824(4)	1.0471(4)	2.4451	0.1920(1)			
TbAg$_{0.9}$Sb$_2$[d]	800	0.42821(5)	1.0475(3)	2.4463	0.1920(1)			
TbAg$_{0.8}$Sb$_2$[d]	800	0.42806(7)	1.0471(2)	2.4461	0.1918(1)			
DyAgSb$_2$	600	0.42733(9)	1.0453(5)	2.4462	0.1909(1)	12.0	−12	10.5
HoAgSb$_2$	600	0.42665(6)	1.0427(4)	2.4440	0.1898(1)	6.0	−6	10.3[c]
ErAgSb$_2$	800	0.42541(8)	1.0413(5)	2.4478	0.1884(1)	4.8	−6	9.4
ErAg$_{0.7}$Sb$_2$[d]	800	0.42552(9)	1.0421(6)	2.4490	0.1886(1)			
TmAgSb$_2$	600	0.42481(6)	1.0395(6)	2.4469	0.1876(1)	3.1	−8	7.5

Note. Error limits on T_N, Θ_p, and μ_{eff} are ±0.5 K, ±1 K and ±0.05 μ_B, respectively.
[a] Noncolinear antiferromagnetism, remanent magnetization $\mu = 0.15\mu_B$/Ce.
[b] $\chi_0 = 1.8 \times 10^{-6}$ cm^3 g^{-1}.
[c] Corrected for ~15 mole% of excess free (Sb) in the alloy.
[d] From multiphase sample.

veal a two-phase mixture: (Sb) and *RE*AgSb, *RE* = Yb, Lu, with the TiNiSi type. The plot of the unit cell dimensions of the isostructural phases *RE*AgSb$_2$ in Fig. 1 merely reflects the lanthanoid contraction. There is no particular deviation from the general trend for the cerium-containing compound, suggesting a typical magnetic behavior of tri-positive cerium (see below). As usual, the volume of the yttrium-containing compound (see Fig. 1) is found between the values for the corresponding Tb and Dy phases.

3.3. Crystal Chemistry

The *RE*AgSb$_2$ compounds are typical representatives of the ZrCuSi$_2$ type which exhibits a remarkably widespread range of isotypic member phases (6). The crystallographic descriptions of the "prototype" compounds such as

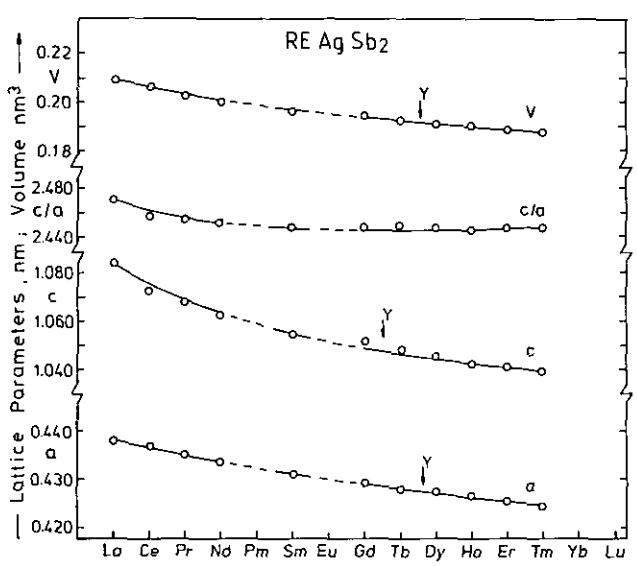

FIG. 1. Lattice parameters and volumes of the compounds *RE*AgSb$_2$.

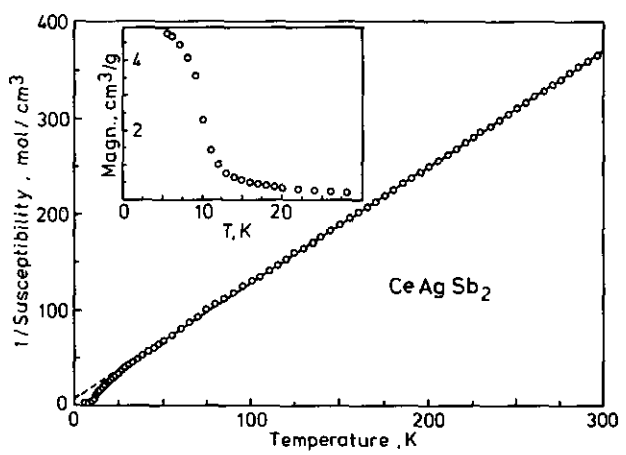

FIG. 2. Molar reciprocal susceptibility versus temperature for CeAgSb$_2$; inset, magnetization versus temperature.

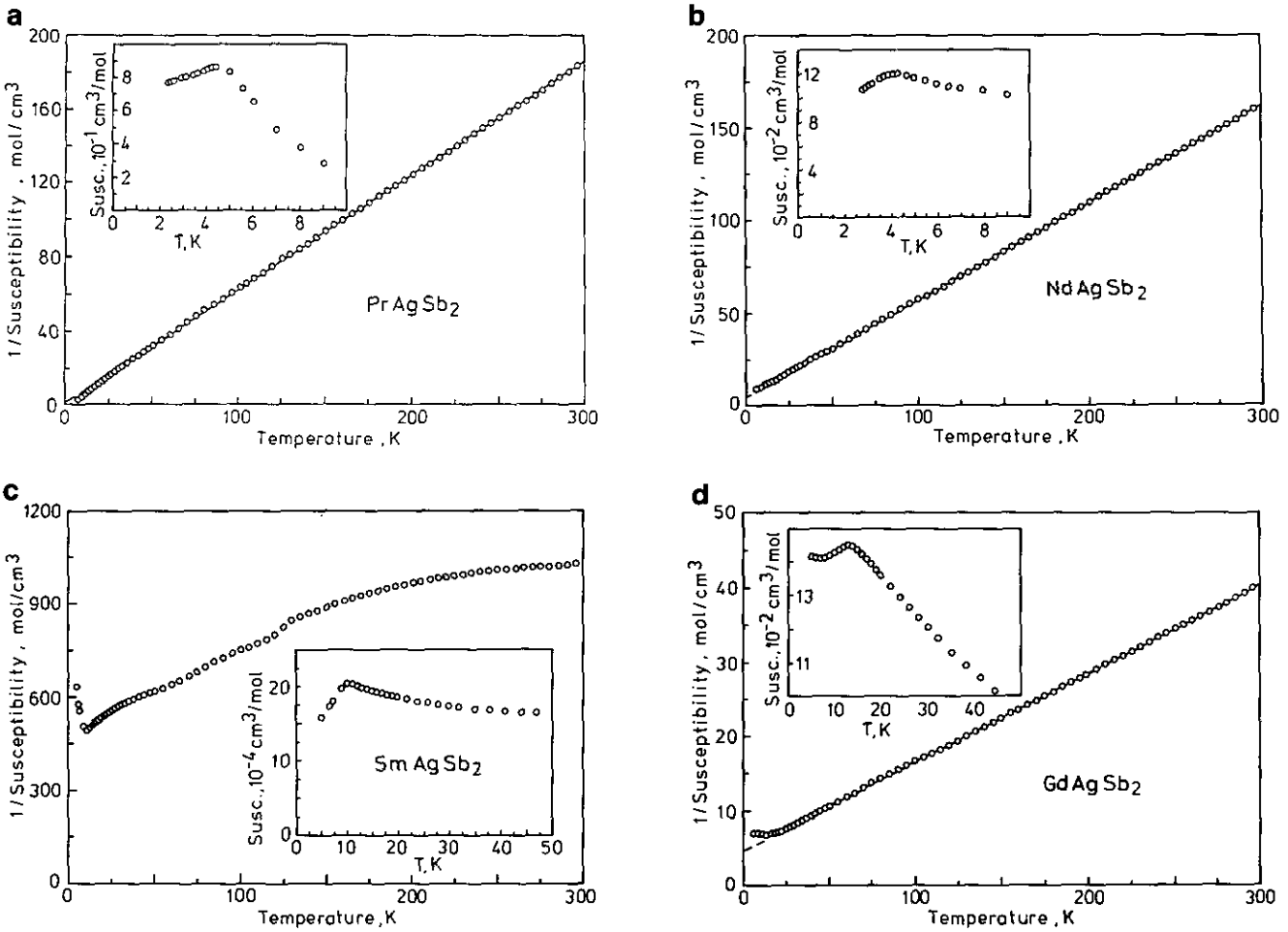

FIG. 3. Molar Susceptibility and reciprocal molar susceptibility (inset) for $PrAgSb_2$ (a), $NdAgSb_2$ (b), $SmAgSb_2$ (c), $GdAgSb_2$ (d), $TbAgSb_2$ (e), $DyAgSb_2$ (f), $HoAgSb_2$ (g), $ErAgSb_2$ (h), and $TmAgSb_2$ (i).

$ZrCuSi_2$, ZrCuSiAs, $UCuAs_2$, $CaMnBi_2$, or $NdFeSb_2$, however, rarely used a consistent set of atom parameters, and in some cases the noncentrosymmetric setting of the tetragonal unit cell was favored (6). The crystallographic analysis of these sets of atom parameters unambiguously proved isotypism among the various descriptions which all can be transferred into each other by simple shifts of the unit cell origin. Therefore a standardized set of atom coordinates has been selected employing the program routine STRUCTURE TIDY (7). The so-obtained set refers to the centrosymmetric choice of origin at center and is given in Table 2. Thus there is no difference between the $UCuAs_2$ (8) and the $ZrCuSi_2$ types, as earlier claimed by Stepien-Damm *et al.* (8).

3.4. Magnetism

Magnetism was generally monitored in the temperature range from 2.5 K to 300 K and results of susceptibility and magnetization measurements are collected in Table 3 and in Figs. 2 and Figs. 3a to 3i. $REAgSb_2$, RE = Y, La, exhibit weakly temperature-dependent paramagnetism. All the compounds with magnetic rare earths were found to exhibit long-range magnetic order at low temperature. The susceptibility curves for RE = Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, and Tm show maxima at temperatures between 3.1 and 14 K, indicating antiferromagnetic ordering of the RE sublattice. The cerium compound $CeAgSb_2$ was found to exhibit weak ferromagnetism below $T_c \sim 12$ K, with a value for the magnetization reaching 0.5 μ_B/Ce under 2 T, and a remanent magnetization of 0.15 μ_B/Ce at 5 K. The paramagnetic Curie temperature is negative ($\Theta_P = -6$ K), so that this weak ferromagnetism probably results from a slightly canted antiferromagnetic structure.

The Van Vleck type paramagnetic susceptibility of $SmAgSb_2$ is typical for the narrowly spaced Sm multiplet intervals and was fitted according to the modified Curie–Weiss law: $\chi = \chi_0 + C/(T - \Theta_P)$ neglecting the small peculiarities at 50 and 10 K (crystal field effects). The susceptibility for all the other RE compounds could be fitted using the simple Curie–Weiss law, giving values for

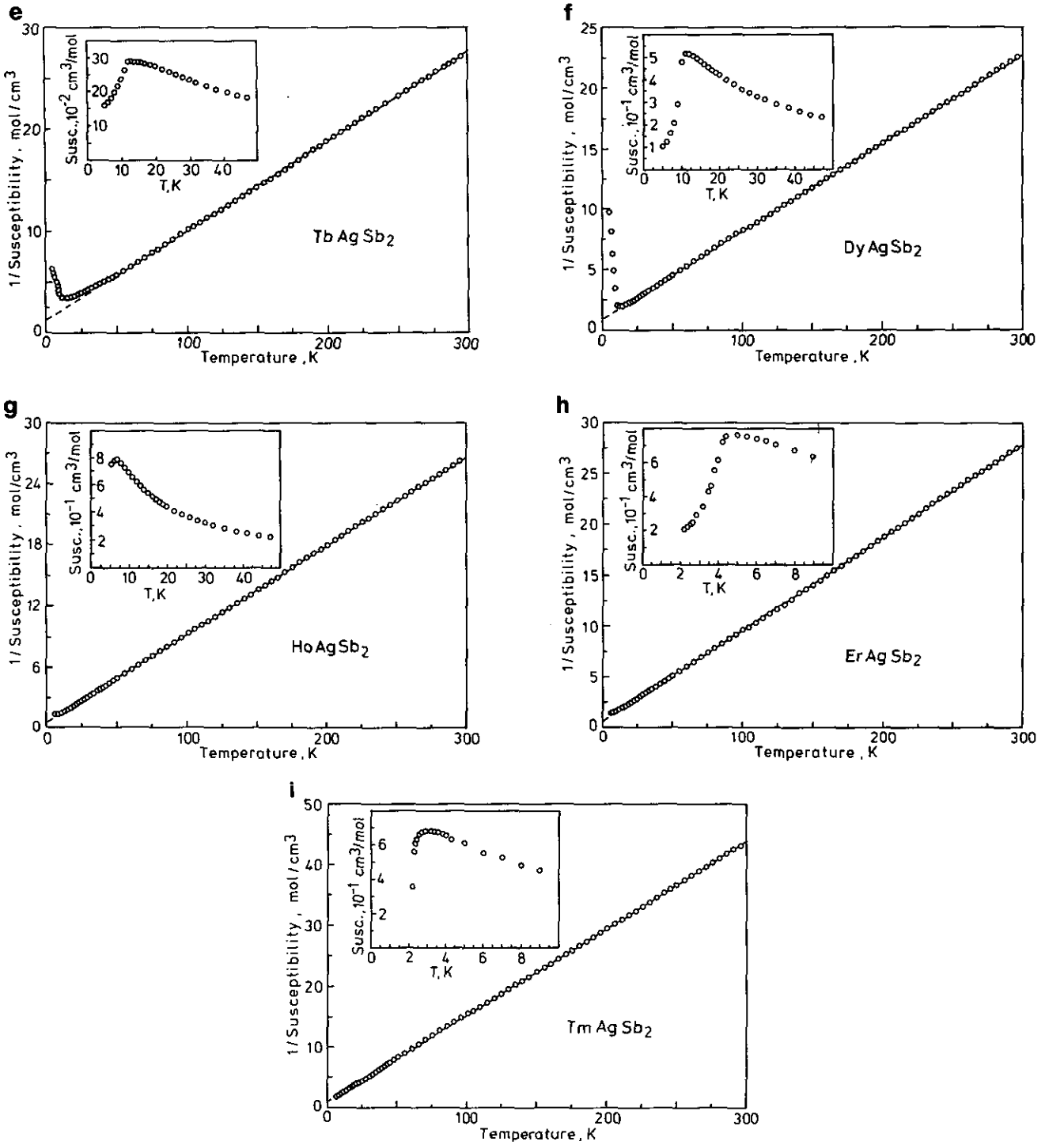

FIG. 3—*Continued*

the paramagnetic moments, in good agreement with that for the trivalent states.

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