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Magnetic and some thermal properties of chalcogenides of Pr and Tm and a few other rare earths

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The magnetic properties of all known sulfides, selenides, and tellurides of Pr and Tm (as representative of the light and heavy rare earths, respectively) have been studied. In most cases, Pr and Tm compounds exhibit Van Vleck paramgnetism at low temperatures owing to crystal-field singlet ground states. Splittings have been derived in several cases by specific-heat measurements. In the case of Pr_3X_4 (X = S, Se,Te) compounds, specific-heat and susceptibility measurements reveal exchange-induced ferromagnetism. This is further supported by the study of the magnetic phase diagrams of Pr_3Se_4-Pr_2Se_3, La_3Se_4-Pr_3Se_4, and of superconductivity in the $(La_{1-x}Pr_x)_3(S_4,Se_4,Te_4)$ series. Superconductivity persists to very high Pr concentrations, as in the $La_{1-x}Pr_xSe$ system, indicating a nonmagnetic ground state of Pr. The higher chalcogenides appear to exhibit in general semimetallic or semiconducting behavior, while most of the metallic La compounds are usually superconductors.

I. INTRODUCTION

Systematic studies of physical properties (especially magnetism) of rare-earth chalcogenides have so far been limited mostly to the simple LnX compounds[1-14] having the rocksalt structure. In the last decade, however, a number of structural studies of other Ln-X phases have become available.[15] Our interest in Pr and Tm chalcogenides arose mainly from their potential application for hyperfine-enhanced nuclear cooling as well as the study of combined electron-nuclear ordering phenomena at very low temperatures.[16] Furthermore, some of these compounds (Pr_3X_4 and TmS) exhibit so-called induced-moment ordering.[17] In these cases the exchange forces compete with the crystal-field energy and one can observe a spontaneous polarization of the singlet ground state below a well-defined ordering temperature. The dynamics of this type of magnetic order have been studied theoretically[18-26] but little work has been done experimentally.[27-30] Interesting effects have also been predicted by Peschel and Fulde[31] in transport properties, such as thermoelectric power, in singlet-ground-state materials. Finally, electronic properties of Pr and Tm chalcogenides are to date widely unknown. A number of these compounds exhibit intermediate valence states,[17] the simplest of which are TmSe and TmTe, but even their properties are not well understood. Preliminary results[17] indicate that the higher polychalcogenides exhibit predominantly semiconducting or semimetallic behavior. This paper, however, is mostly concerned with the magnetic properties of all the chalcogenides, excluding the oxides. A preliminary review has been given previously.[17,32]

II. EXPERIMENTAL PROCEDURE

A. Sample preparation

Appropriate amounts of rare-earth metals and S, Se, or Te were doubly sealed in quartz tubes. Rare-earth metals were used in the form of turnings made on a lathe in order to obtain a good preliminary reaction product. Double sealing was done as a preventive measure against excessive contamination with oxygen or nitrogen, whose diffusion coefficients through quartz become appreciable at temperatures above 900–1000 °C. Following a reaction time of 2–3 days up to 1150 °C, the material was subsequently crushed (in dry nitrogen gas, where necessary) in an agate mortar. Usually the first reaction product is multiphase material at this stage. For congruently melting materials (such as PrX, Pr_3X_4, TmX, Tm_2Se_3, Tm_3Se_4, Tm_2Te_3) the fine powder was subsequently transferred into a tantalum tube ($\frac{1}{4}$–$\frac{1}{2}$ in., 6–10-mil wall) with its ends squeezed in high-current clamps and then melted by resistance heating in 10^{-6} Torr. Severe outgassing was often observed and, together with the effect of directional solidification, a noticeable purification can be expected by this process. In cases where no congruent melting occurs (e.g., Pr_2Se_3, $PrSe_2$, Pr_2Te_5, etc.), the first reaction product was powdered and pressed into pellets and rereacted for several days at appropriate temperatures. In a few unique cases, the compounds richest in chalcogen elements (e.g., PrS_2, Pr_3Se_7, $PrTe_3$, $TmTe_3$, etc.) were obtained by dissolving the first reaction product in large amounts of S, Se, or Te and kept for 10–14 days slightly below the decomposition temperature in the liquid chalcogen, the material being at the cold end in a temperature gradient. After this time the excess of S, Se, Te was distilled off by reversing the temperature gradient. Relatively large single crystals can be grown easily this way (except PrS_2). Strongly anisotropic structures such as $PrTe_3$ and $TmTe_3$, however, only yielded long flakes of approximately $0.5 \times 3 \times 15$ mm. The fact that the chalcogenide phases exhibit a large variety of colors is a help in quickly identifying the correct phase, usually confirmed by x rays and magnetic tests. One of the most serious difficulties in obtaining single-phase material was the often incredible amount of gaseous impurities (H, N, O, and hydrocarbons) present in the starting material, in many cases up to 5 at. %. In general, Lunex rare earths (Lunex, Pleasant Valley, Iowa) were found to be by far the least contaminated with gases and yielded the most reproducible results.

B. Magnetic measurements

These measurements were performed in three different ways: Ordering or superconducting temperatures were detected by a standard ac mutual-inductance method in fields of 0.5–10 Oe. Susceptibilities between 1.3 and 400 K were measured in a pendulum magnetometer in fields between 1.25 and 15 kOe. Magnetization or resistivity curves were taken in fields up to 60 kOe generated by a superconducting solenoid. The magnetization was detected by transforming the sample flux to a location outside the superconducting solenoid (but still in the 4.2-K He bath) by means of a superconducting flux transformer and monitoring it with a flux-gate magnetometer.

C. Specific heat

The specific-heat data were taken in a heat-pulse calorimeter, described earlier.[33] By this method small samples (about 0.05–0.1 cm^3) can be measured. This is particularly important, since most of the chalcogenides which could be melted were extremely brittle and broke into small pieces after cooling in the Ta crucible.

III. RESULTS

Tables I–VIII summarize all our experimental results. We feel it is convenient to discuss the compounds in groups related to the same physical problems. In Tables VII and VIII we present some data of compounds with rare earths other than Pr and Tm. They were mainly used to derive or to clarify some of the basic properties of the analogous Pr or Tm compounds, and we will discuss some of them first.

A. La, Y, and La-Y compounds

The La monochalcogenides are superconductors near 1 °K and the superconducting transition temperatures T_c, as well as the electronic specific heats γ, increase from the monosulfide to the monotelluride. The correlation between T_c and γ still persists in the metallic La_3X_4 compounds with Th_3P_4 structure although in these compounds the sulfide has the highest values. The relatively large electronic specific heat indicates that the Fermi level is located in the 5d band. In the monochalcogenides, the increase from the sulfide to the telluride can be easily understood on the basis of Methfessel's band-structure scheme.[1] We ex-

TABLE I. Pr–S compounds.

Comp.	Struct.	Lattice[a] const. (Å)	T_C (K)	T_N (K)	$\chi(0)$ (cm^3/mole)	Other properties
PrS	NaCl	5.735			0.0216	golden metal, $H_{hf}/H_0 = 5.84$, $A_4 \langle r^4 \rangle = 13.3$ meV, $A_6 \langle r^6 \rangle = 0.79$ meV (Ref. 36)
Pr_3S_4	Th_3P_4	8.573	$\lesssim 7.1$			black-purple metal induced-moment system $\mu_{sat} \sim 0.5 \mu_B/Pr^{3+}$, resist. anomaly at 45 K[c]
α-Pr_2S_3	ortho-rhomb.	$a = 7.49$[b] $b = 4.10$ $c = 15.69$		2.48		brown semiconductor
β-Pr_2S_3	quadratic	$a = 15.10$[b] $c = 20.05$		1.07		green semicond. possibly $Pr_{10}S_{14}O$ (Ref. 60)
γ-Pr_2S_3	Th_3P_4	8.573			0.0615	orange semiconductor
PrS_2	cubic	8.06			0.0259	light-brown semiconductor, complex NMR pattern with field-dep. linewidth

[a] This work unless reference given.

[b] Reference 60.

[c] See *Note added in proof*.

TABLE II. Pr-Se compounds.

Comp.	Struct.	Lattice[a] const. (Å)	T_C (K)	T_N (K)	$\chi(0)$ (cm^3/mole)	Other properties
PrSe	NaCl	5.947			0.0254	red-golden metal, $H_{hf}/H_0=5.52$, $A_4\langle r^4\rangle=12.7$ meV, $A_6\langle r^6\rangle=0.42$ meV (Ref. 36)
Pr_5Se_6(?)	?		(14.3?)			deep-purple metal
Pr_3Se_4	Th_3P_4	8.895	$\lesssim 19$			intense blue metal, induced-moment syst., $\mu_{sat}\sim 1\mu_B/Pr^{3+}$, resist. anomaly at ~30 K and T_c two anomalies: 14.3 and 17–19 K in low-field susceptibility[b]
Pr_2Se_3	Th_3P_4	8.904			0.0564	brick-red semiconductor
Pr_4Se_7	tetrag.	$a=8.44$ $c=8.49$			0.0498	brown semiconductor
$PrSe_2$	ortho-rhomb.	$a=16.40$ $b=16.78$ $c=12.34$			0.0282	gray-silver semiconductor
Pr_3Se_7	tetrag.	not anal.			0.0312	light-gray-green semiconductor

[a]This work unless reference given.

[b]See *Note added in proof.*

pect a narrowing of the 5*d* band from the sulfide to the telluride owing to reduced overlapping of the 5*d* wave functions. Filling the band with the same number of conduction electrons (one per formula unit) we expect the density of states to go up. The Th_3P_4 structure type exists only among the light rare-earth chalcogenides. For Y, only Y_3Se_4 exists, but in a different structure type. However, the Th_3P_4 structure can be obtained under high pressure, as for all the heavy rare earths.[34] We attempted to investigate the possibility of high superconducting transition temperatures of Y_3X_4 in

TABLE III. Pr-Te compounds.

Comp.	Struct.	Lattice[a] const. (Å)	T_C (K)	T_N (K)	$\chi(0)$ (cm^3/mole)	Other properties
PrTe	NaCl	6.320			0.0374	deep-purple metal, $H_{hf}/H_0=7.78$, $A_4\langle r^4\rangle=9.4$ meV, $A_6\langle r^6\rangle=0.15$ meV (Ref. 36)
Pr_3Te_4	Th_3P_4	9.490	$\lesssim 7.8$			silver-blue metal, induced-moment system, $\mu_{sat}\sim 0.75\mu_B/Pr^{3+}$
Pr_2Te_3	Th_3P_4	9.479			0.0534	silver-gray semiconductor
Pr_4Te_7	tetrag.	$a=8.858$ $c=9.064$			0.0714	silvery semiconductor
$PrTe_2$	anti-Fe_2As	$a=4.459$ $c=9.072$			0.042	black-purple, semimetal?
Pr_3Te_7	not anal.	not anal.			0.044	bright-silver semiconductor
Pr_2Te_5	tetrag.	$a=4.426$[b] $c=44.3$			0.0288	dark-red–golden semiconductor
Pr_4Te_{11}	not anal.	not anal.			0.0240	red-golden semiconductor
$PrTe_3$	$NdTe_3$	$a=4.461$ $c=25.86$			0.0230	red-golden micaceous semiconductor, unstable in air

[a]This work unless reference given.

[b]Reference 15.

TABLE IV. Tm-S compounds.

Comp.	Struct.	Lattice[a] const. (Å)	T_N (K)	$\chi(0)$ (cm^3/mole)	Other properties
TmS	NaCl	5.420	5.18		golden metal, $\rho(300\ \mathrm{K}) = 100$ $\mu\Omega$ cm, ρ_{max} at 14 K of 177 $\mu\Omega$ cm, $P_{\mathrm{eff}} = 7.19$, indication of valence instability
Tm_5S_7	mono-clinic	$a = 12.628$[b] $b = 3.761$ $c = 11.462$ $\beta = 104.82°$	~0.6		black metal
Tm_2S_3	Tl_2O_3	$a = 10.51$[c]	< 0.5		yellow, probably Van Vleck paramagnetic
δ-Tm_2S_3	mono-clinic	not det.	< 0.5		yellow, probably Van Vleck paramagnetic

[a]This work unless reference given. [b]Reference 15. [c]Reference 65.

the Th_3P_4 structure. Solid solutions of $(La_{1-x}Y_x)_3X_4$, however, revealed a rapid drop in the superconducting transition temperature and electronic specific heat, and most likely Y_3X_4 will not exhibit high superconducting transition temperatures, even when stabilized in the Th_3P_4 structure. Y_3Se_4 in the rhombohedral phase shows an extremely low electronic specific heat. It is not even clear at present whether Y_3Se_4 is intrinsically a metal. The strong change of slope in the C/T-vs-T^2 plot could be due to magnetic impurities or implies an unusually strong variation of the Debye temperature below 5 K. The superconductivity of the LaX and La_3X_4 compounds is also a most welcome property to test recent theories of Fulde *et al.*[23,35] concerning superconductors doped with impurities in a nonmagnetic crystal-field ground state. These systems offer the possibility of detecting crystal-field levels by tunneling spectroscopy. Crystal-field splittings of corresponding PrX compounds have recently been thoroughly investigated,[36] and shown to be a key parameter in the behavior of such superconductors.[23,35] In Fig. 1 we show superconducting transition temperatures of $La_{1-x}Pr_xSe$, $(La_{1-x}Pr_x)_3S_4$, and $(La_{1-x}Pr_x)_3Se_4$. The persistence of superconductivity up to such large values of x is indicative of a nonmagnetic crystal-field ground state of Pr in all three cases, as demonstrated previously.[28,37] This is in full agreement with the fact that the ferromagnetic Pr_3X_4 compounds are exchange-induced-moment systems (as we will show in III D).

B. PrS, PrSe, PrTe

All these compounds are metallic Van Vleck paramagnets, with a singlet Γ_1 as crystal-field

TABLE V. Tm-Se compounds.

Comp.	Struct.	Lattice[a] const. (Å)	T_N (K)	$\chi(0)$ (cm^3/mole)	Other properties
TmSe	NaCl	5.64–5.71	1.85–2.8	0.38[c]	red-brown color, intermediate-valence system, $P_{\mathrm{eff}} = 6.32$, $\rho(300\ \mathrm{K}) = 700$ $\mu\Omega$ cm, $d\rho/dT < 0$, $d\rho/dp = -4.9$ $\mu\Omega$ cm/kbar (Ref. 52)
Tm_5Se_6	rhombo-hedral	5.63	2.1		deep purple
Tm_3Se_4	rhombo-hedral	5.64		0.535	dark blue, congr. melting, possibly semiconductor
Tm_2Se_3	Sc_2S_3	$a = 11.31$[b] $b = 8.06$ $c = 24.06$		0.305	brown-red semiconductor

[a]This work unless reference given. [b]Reference 15. [c]Reference 49.

TABLE VI. Tm-Te compounds.

Comp.	Struct.	Lattice[a] const. (Å)	T_N (K)	$\chi(0)$ (cm^3/mole)	Other properties
TmTe	NaCl	6.049[b]–6.364	0.21		silver-blue semiconductor, ρ(300 K) ~10–50 Ω cm, cont. semiconductor-metal transition under pressure [−10 meV/kbar (Ref. 3)]
Tm_2Te_3	Sc_2S_3	a = 12.09[c] b = 8.55 c = 25.65		0.451	light-green semiconductor, very unstable in air
$TmTe_3$	$NdTe_3$	a = 4.274 c = 25.34	~0.6?		red-golden semiconductor, P_{eff} ~6.0 (possibly mixed valence state), very unstable in air

[a] This work unless reference given. [b] Reference 50. [c] Reference 15.

ground state.[4,36] Together with the Pr monopnictides they belong to a group of compounds in which the effective point-charge model works very well.[36] We have been unable to verify an ordering temperature of 16 K reported for PrS.[5,13] NMR of the Pr nucleus was observed at He temperatures, confirming the absence of magnetic order in PrS. Values of the hyperfine-field enhancement factors (1 + K) given in Table I agree well with calculated values from susceptibility data,

$$\frac{H_{\mathrm{hf}}}{H_o} \equiv 1 + K = 1 + \frac{a\chi(0)}{g_N \mu_N g_J \mu_B} , \qquad (1)$$

except for PrS, where some discrepancy could not be removed, and measured values from NMR are somewhat higher than given by (1).

Qualitatively, nuclear cooling effects have been observed in PrSe and PrTe. Since the hyperfine enhancement factors $1+K$ are not very large in these Van Vleck paramagnets, the cooling efficiency (or the amount of nuclear entropy removed at a given temperature and field) is not exceptionally large either. The usefulness of the PrX compounds for nuclear cooling experiments may further be hampered by the possible presence of traces of the neighboring Pr_3X_4 phases which order magnetically and may introduce thermodynamic irreversibilities in the demagnetization process. Metallic Van Vleck paramagnets containing Pr ions often exhibit nuclear magnetic order above 1 mK due to residual exchange interactions. In PrS (and also in $PrBe_{13}$[38]) these seem to be especially small. Taking into account the moderate magnitude of the enhancement factor, one would expect no nuclear

TABLE VII. Other related nonmagnetic chalcogenides.

Comp.	Struct.	Lattice const. (Å)	T_c (K)	γ (mJ/°K^2 mole)[a]	$\Theta_D(0)$ (K)	Other properties
LaS	NaCl	5.856	0.84	3.28	276	
LaSe	NaCl	6.060	1.02	3.77	231	
LaTe	NaCl	6.421	1.48	4.65	175	
La_3S_4	Th_3P_4	8.730	8.06	~7.2	230	$C_{es}/\gamma T_c$ = 2.85
La_3Se_4	Th_3P_4	9.060	7.80	~6.3	195	$C_{es}/\gamma T_c$ = 2.90, resist. anomaly at 62 K
La_3Te_4	Th_3P_4	9.630	5.30	~4.3	162	$C_{es}/\gamma T_c$ = 2.70
LaS_2	cubic	8.19				diamagn. light-brown semiconductor
Y_3Se_4	ortho-rhomb. Sc_2S_3	5.725 (NaCl subcell)[b]	< 0.35	≲0.7	274	(possibly semiconductor)
$(La_{0.8}Y_{0.2})_3S_4$	Th_3P_4	8.670	4.77	6.2	252	
$(La_{0.8}Y_{0.2})_3Se_4$	Th_3P_4	9.004	3.92	4.5	221	
$(La_{0.8}Y_{0.2})_3Te_4$	Th_3P_4	9.586	< 1.7	2.1	208	

[a] Per mole of transition metal. [b] Reference 15.

TABLE VIII. Other related magnetic chalcogenides.

Comp.	Struct.	Lattice const. (Å)	T_N (K)	θ_p (K)	Other properties
NdS_2	nearly cubic	8.03	2.20		light-brown semiconductor
TbS	NaCl	5.515	49	−88	bright-golden metal
TbSe	NaCl	5.726	52	−73	red-golden metal
TbTe	NaCl	6.102	63	−65	deep-purple metal

order above 0.3 mK in PrS. Depending on the quality of the sample and of the thermal contact that can be made to it, PrS may possibly prove useful for magnetic cooling to below 1 mK.

C. TmS, TmSe, TmTe

These compounds are expected to exhibit a crystal-field singlet ground state,[39] from comparison with a recent study of rare-earth pnictides[40] and other rare-earth monochalcogenides.[4,17,36] The results, however, are considerably different from such an expectation. All three compounds, TmS, TmSe, and TmTe, exhibit magnetic phase transitions at 5.2, 1.85, and 0.21 K, respectively. The first two are clearly seen in the specific-heat curves shown in Fig. 2, whereas TmTe shows a flat maximum near 6 K, presumably due to crystal-field levels. Unfortunately, several attempts to measure crystal-field splittings in Tm*X* compounds[41] were unsuccessful. We believe that this is an inherent difficulty of Tm monochalcogenides and reflects the basic instability of the 3+ valence state in these compounds. The indetectability of crystal-field splittings may have three basic causes: (i) Whenever unstable valence states occur, the Fermi level is close to the 4*f* level. In this case crystal-field splittings may be anomalously small, as shown in a systematic study of rare-earth pnictides.[40] Ce, for example, exhibits crystal-field splittings about an order of magnitude smaller than expected.[40] (ii) If fluctuations between both valence states are comparable or even faster than the characteristic inverse frequency of a thermal neutron (~ 10^{-12} sec) no splitting can be detected. (iii) In ordering compounds, crystal-field level dispersion may be so strong that they can no longer be detected.

It is very difficult to discriminate between these various possibilities. From the specific-heat data we find that in TmS the electronic entropy $(1/R)\int_0^{T_N}(C_m/T)dT$ corresponds to about ln 1.6. This would yield a Γ_1-Γ_4 splitting of about 16 K in a molecular-field approximation. In general, this value is low by as much as a factor of 2. On the other hand, from dilute $Lu_{1-x}Tm_xS$ systems we find a Γ_1-Γ_4 splitting of 32 K (for $x = 0.05$ and 0.1).

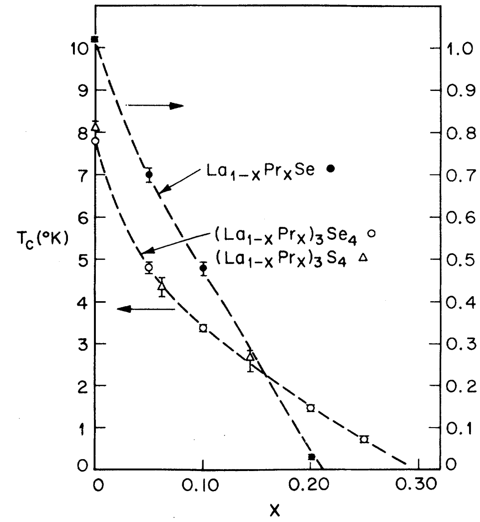

FIG. 1. Superconducting transition temperatures in $La_{1-x}Pr_xSe$, $(La_{1-x}Pr_x)_3S_4$ and $(La_{1-x}Pr_x)_3Se_4$.

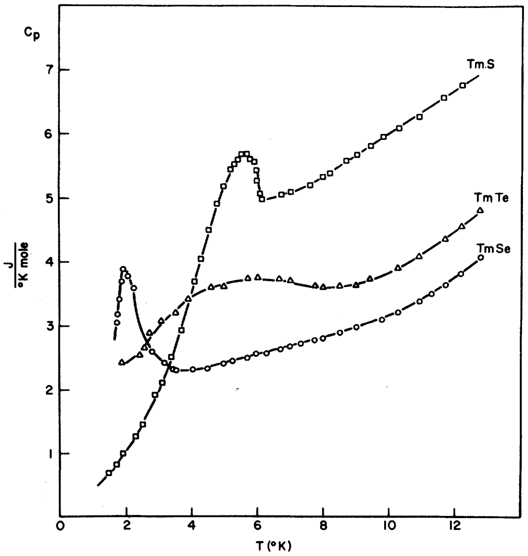

FIG. 2. Specific heat of Tm monochalcogenides between 1.7 and 15 K.

These splittings do not necessarily have to agree, but empirically we found in numerous systems that dilution of a magnetic rare-earth ion in a corresponding La or Lu compound does not change crystal-field splittings by more than a few percent. A point-charge calculation would yield a Γ_1-Γ_4 splitting in TmS of 25 K (assuming $Z = -2$ as appropriate to all Pr monochalcogenides[36]). Thus, there is some evidence that (ii) and/or (iii) are the reason for the failure to detect crystal-field splittings in TmS.

From the specific-heat measurements and the magnetic dilution experiment with LuS, we conclude that TmS is an exchange-induced-moment system, and that the crystal-field ground state must be nonmagnetic, presumably Γ_1. However, the high Néel temperature of 5.2 K is rather puzzling. As previously mentioned, Van Vleck paramagnetism is expected from extrapolation of the strength of the exchange interaction in other trivalent monosulfides (which by the way are following the de Gennes relation quite well) at least as long as the Γ_1-Γ_4 splitting is larger than 6 K. Such a small splitting must clearly be excluded from our specific-heat data and the small entropy $S(T_N = 5.2\text{ K}) = 0.47R$ $(= R \ln 1.6)$. The expected Néel temperature from the de Gennes function in TmS is 5.4 K, very close to the experimental value. Thus it appears that the exchange interaction in TmS is anomalously large, leading us back to the previously suspected incipient valence instability in TmS, presumably being the reason for it. In numerous Ce compounds similar observations can be made: Closeness of the 4*f* level to the Fermi level leads to valence instability or anomalous magnetic order.

The effective moment of 7.19 in TmS indicates indeed a slight reduction compared with a theoretical value of 7.56. However, this number by itself is not convincing. Crystal-field splitting or slight sulfur excess may also at least partially account for it. The valence instability becomes even more evident when considering the whole sequence TmS, TmSe, TmTe, where the transition to a divalent state can be unambiguously seen magnetically and also in the lattice constants. In Fig. 3 we see a plot of lattice constants of monochalcogenides. TmS does not show any deviation although its effective moment is slightly reduced. TmSe, however, does show a slight lattice expansion, corresponding roughly to a valence of ~ 2.8. In contrast, TmTe shows a lattice constant corresponding nearly to the pure divalent state. The same trend is also reflected in the magnetic behavior, shown in Fig. 4. The effective moment drops gradually from TmS to TmTe. In none of the compounds, however, are the theoretical moment values of 7.56 and 4.5 reached for the pure $Tm^{3+}(4f^{12})$ and $Tm^{2+}(4f^{13})$ configurations, respectively.

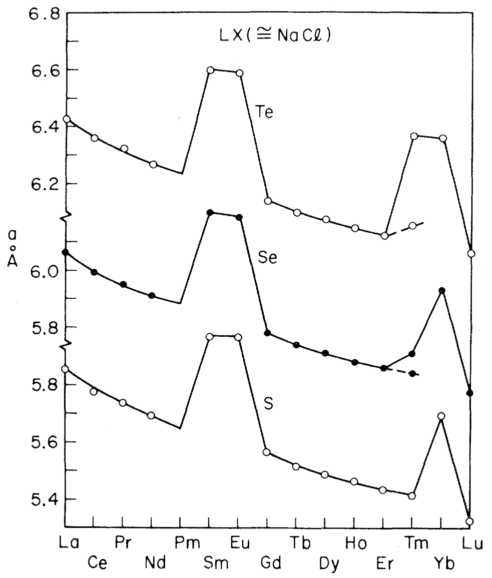

FIG. 3. Lattice constants of monochalcogenides of the rare earths.

The magnetization of TmSe at 1.43 and 4.22 K is shown in Fig. 5. The magnetization curve below T_N is extremely complex and cannot be interpreted straightforwardly. By analogy with Ce compounds we expect transport properties to be extremely sensitive to such a valence instability.

In Fig. 6 we present the temperature dependence of the resistivities of TmS and TmSe (normalized to their room-temperature values). TmS exhibits a pronounced resistance maximum at 14 K with a barely detectable anomaly at its ordering temperature, usually characteristic of exchange-induced-moment systems.[29] TmSe, on the other hand, exhibits a monotonic increase in resistivity with decreasing temperature at least down to 0.5 K, where it reaches a value of $\sim 5 \cdot 10^{-3}\ \Omega\,\text{cm}$. A tempting qualitative explanation may be an increasingly favored divalent state at low temperature, and the increase in resistivity could then be explained by depletion of carriers. The TmS results, however, cannot be explained easily and we will not spend more time on idle speculation unless more experimental data are available to suggest an unambiguous explanation. In Fig. 7 we show on a logarithmic scale the resistivity ρ vs $10^3/T$ for TmTe and again TmSe. On a $1/T$ scale, the behavior of TmSe appears to "level off" at low temperature and no characteristic activation energy can be derived. We meet similar difficulties in TmTe, which, however, behaves much more like a semiconductor, as far as resistivity values are con-

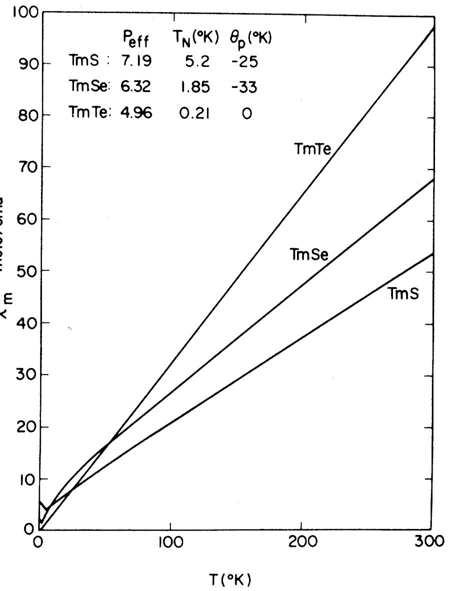

FIG. 4. Inverse molar susceptibility of Tm monochalcogenides between 1.3 and 300 K.

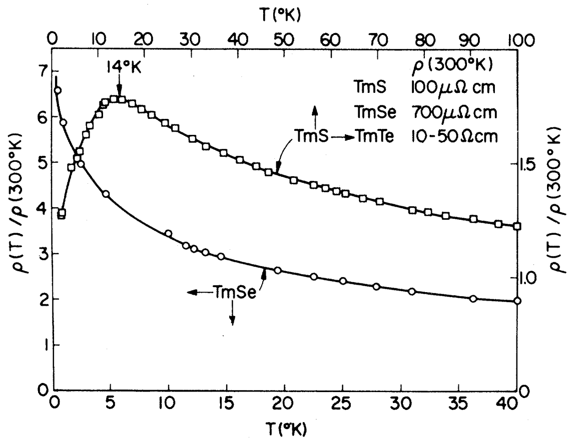

FIG. 6. Relative temperature variation of the resistivity of TmS (upper and right-side scale) and TmSe (lower and left-side scale).

cerned. In an intrinsically clean semiconductor we expect the resistivity at low temperature to follow an expression

$$\rho \sim e^{\Delta/2kT}, \tag{2}$$

where Δ is the activation energy of a $4f$ electron in the Hund's-rule ground state to the bottom of the $5d6s$ conduction band. The slope taken at low temperature yields an activation energy of ~0.11 eV from (2). We have to point out, however, that using (2) leads to difficulties in other semiconducting tellurides, such as SmTe or YbTe. In the latter two we found only agreement with activation energies derived optically or by pressure assuming

$$\rho \sim e^{\Delta/kT}. \tag{3}$$

This means that the Fermi level is pinned down by some trap level, either donor or acceptor impurities, and is not determined by the temperature, i.e., the number of thermally and intrinsically excited carriers (= number of $4f^{12}$ states). From the pressure experiment and (3) we find $\Delta = 0.22$

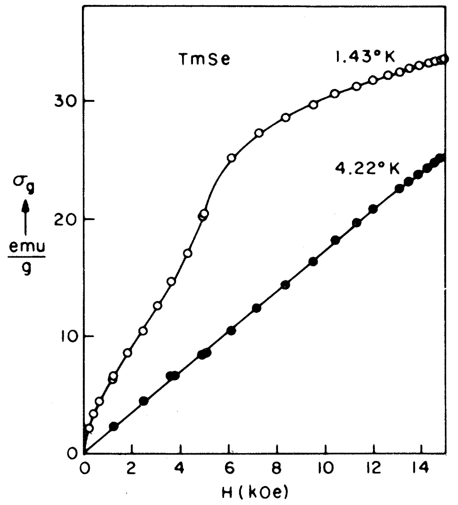

FIG. 5. Magnetization vs field of TmSe at 1.43 and 4.22 K.

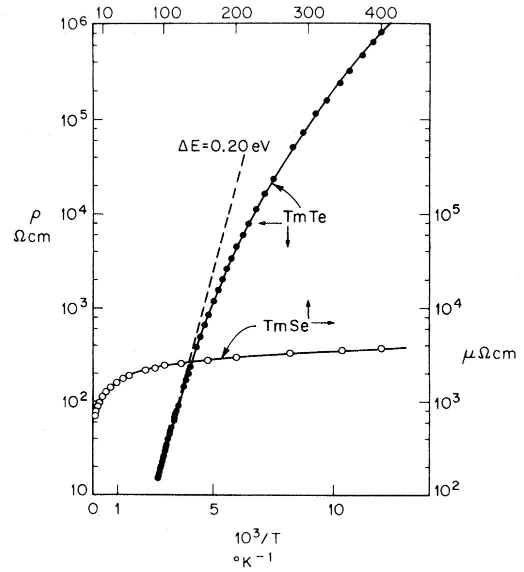

FIG. 7. Log plot of resistivity ρ vs $10^3/T$ of TmTe and TmSe.

eV, for TmTe. We find close agreement with this number by taking the slope in the $\ln\rho - 10^3/T$ plot at room temperature and using (3) again. Thus we are led to believe that the low-temperature deviation from (3) might be due to impurities and/or deviation from stoichiometry. It should be kept in mind, however, that a faster than exponential drop in resistivity with increasing temperature can also have a physical origin and was observed in other semiconducting monochalcogenides such as SmS, SmSe, and SmTe.[42] Part of the explanation in the latter are the low-lying multiplets of Sm^{2+}, having the effect of reducing the effective activation energy Δ. This effect can be excluded in TmTe. The higher multiplets are far too distant to show any effect in our explored temperature range.[42] A second possibility is the gain in Coulomb energy as $5d6s$ carriers are excited (consisting of promoted $4f$ electrons) as in the Falicov-Kimball-Ramirez (FKR) model.[43] This leads qualitatively to a behavior as shown in Fig. 7. A third possible explanation is a recently proposed model by Hirst,[44] called interconfiguration fluctuation, avoiding a serious inconsistency of the FKR model. The mechanism is a spontaneous emission and reabsorption of an f electron occurring at a characteristic frequency given by $\Delta/\hbar$, where $\Delta = \pi |V|^2 N(\epsilon_F)$, and V is a matrix element mixing both states [for TmX: $4f^{12}(5d6s)^1$ and $4f^{13}$]. Typically, Δ is expected to be of the order of a few hundred kelvin. Magnetically it implies that the susceptibility is given by[44]

$$\chi_m = \frac{\langle \mu^2 \rangle}{3kT + \Delta}\ , \tag{4}$$

where $\langle \mu^2 \rangle$ is a weighted average of the squared effective moments in both valence states. At low temperature, (4) is difficult to test because of crystal-field splittings and/or short-range order effects above ordering temperatures. Confronting (4) with experiments we find, however, surprisingly little evidence for the existence of Δ. In Fig. 4 TmTe shows a perfect Curie law, thus $\Delta = 0$. From the relation

$$\langle \mu^2 \rangle = p_{2+} \langle \mu_{2+}^2 \rangle + p_{3+} \langle \mu_{3+}^2 \rangle \tag{5}$$

and the relation $p_{2+} + p_{3+} = 1$ we find $p_{2+} = 0.88$ for TmTe and correspondingly 0.47 and 0.15 for TmSe and TmS. These values are in rather poor agreement with numbers derived from other properties. From lattice-constant considerations, e.g., we expect $p_{2+} \approx 0.93$ for TmTe and 0.22 and ~ 0 for TmSe and TmS, respectively. Unfortunately we have no answer for this problem at the present time.

Compared to other compounds in an intermediate valence state, the Tm*X* series behaves rather differently. It is well known for numerous Ce or Yb compounds that no magnetic order occurs and that the atomiclike $4f$ levels tend to delocalize and behave more like very narrow bands with high and strongly temperature-dependent densities of states.[45] This was recently found for systems with more than one $4f$ electron or hole, e.g., SmS,[46] SmB_6.[47] In our case, there is no evidence for such a delocalization effect. TmSe, for example, orders in an intermediate valence state. It is difficult to understand a magnetic phase transition in such a state. One may ask here whether in TmSe we have magnetic order due to the Kramers $4f^{13}$ state or exchange induced magnetic order in the $4f^{12}$ non-Kramers state, in which we expect a Γ_1 crystal-field singlet lowest, or even a coupled order of both. A similar phenomenon has been observed by Wohlleben *et al.*[48] in TmTe under pressure. They found a susceptibility maximum near 1 K in the partially collapsed phase corresponding roughly to TmSe at zero pressure. On the other hand, Jones[49] has indeed shown by hyperfine enhanced NMR that the crystal-field ground state in $Tm^{3+}Se$ is indeed Γ_1 and that this compound is Van Vleck paramagnetic. It is interesting to note that the stability of the valence state is quite critically dependent on Se or Te concentration. Iandelli[50,51] and Jones[49] have obtained trivalent TmSe by reaction of Tm filings in Se vapor at low temperature. In this work we have found that slight excess of Te or Se causes a noticeable contraction of the lattice constant and thus favors the trivalent state of Tm. In Fig. 3 we have also plotted the limiting lattice constants of TmSe and TmTe which can be obtained by slight excess of Te. These numbers agree very well with Iandelli's[50,51] data. At higher Se concentrations corresponding to Tm_5Se_6 a new superstructure of the NaCl cell appears[15] which orders at about the same temperature as TmSe, but which is much closer to the 3+ state. On the other hand we found that TmSe shows a relatively high compressibility. At pressures between 0 and 43 kbar it shows a linear drop in resistivity of $-4.9\,\mu\Omega\,\mathrm{cm}/\mathrm{kbar}$[52] at room temperature. The phase transition vs pressure is continuous as in TmTe[53] and in the collapsed phase of SmS.[46] Even at 43 kbar it appears that TmSe is not yet in the fully trivalent state.

In conclusion, it is evident that the Tm*X* compounds are perhaps one of the most unique series of compounds to use in the study of the properties of unstable valence systems at various stages, and recent preliminary results of soft-x-ray photoemission studies fully confirm it.[54]

D. $Pr_2X_3 - Pr_3X_4$

These systems have some rather unique features which were the driving force for their exploration.

First of all, they are expected to show a continuous transition from the metallic Pr_3X_4 to the semiconducting Pr_2X_3[55–59] (for all X, i.e., S, Se, Te) without change in lattice constants. A complication does occur for the sulfide, where two other low-temperature phases of Pr_2S_3 (α and β) have been reported.[15] The β phase is probably stabilized by traces of oxygen.[60] However, the Th_3P_4 phase of Pr_2S_3 (γ-Pr_2S_3) can easily be obtained at 1300 °C[15] and is stable against any phase transformation down to liquid-He temperatures. γ-Pr_2S_3 is Van Vleck paramagnetic whereas α- and β-Pr_2S_3 order antiferromagnetically. Ferromagnetism of purely trivalent L_3X_4 phases has been found by Holtzberg *et al.*,[55] Starovoitov *et al.*,[61] and Novikov and Shalit.[62] Ferromagnetic properties in Pr_3X_4, however, have not yet been reported. All our measurements indicate that Pr is in a crystal-field singlet ground state, in agreement with conclusions drawn from the superconducting $(La_{1-x}Pr_x)_3X_4$ systems (see III A): (i) T_c of Pr_3X_4 is considerably lower than in the corresponding neighboring Ce_3X_4[61,62] and Nd_3X_4[62] compounds, (ii) the specific heat shows a very weak anomaly at the Curie temperatures (see Fig. 8), and (iii) resistivity measurements were performed in Pr_3S_4 and Pr_3Se_4 and show characteristic features of induced-moment systems.[29] The Curie temperatures are indicated by a barely detectable slope change in a ρ-vs-T plot and in both compounds the resistivity shows an appreciable temperature variation down to 1 K, presumably due to low-lying exciton modes.[18,29] Several samples of Pr_3S_4 showed a pronounced anomaly at 45 K as shown in Fig. 9, indicating a possible structural instability. In La_3Se_4 a similar anomaly was found at 62 K. Their common features are that they only occur in good crystals with perfect stoichiometry. Excess of S or Se destroys the transition. Pr_3Se_4 shows a pronounced change in slope at 30 K. If interpreted as a crystal-field effect, one expects a splitting of the lowest levels of approximately 60 K. (iv) T_c in all Pr_3X_4 compounds drops rapidly to zero upon dilution with La (see Fig. 10). The analysis of the phase diagram shown in Fig. 10 follows the La_3Tl-Pr_3Tl system[28] and will not be discussed here further. (v) T_c drops sharply upon depletion of carriers going over to Van Vleck paramagnetism (Fig. 11). The latter property is perhaps the most instructive and interesting one of all. The Pr_3X_4-Pr_2X_3 system should actually be written as a ternary, including Pr vacancies v: $Pr_{12-x}v_xX_{16}$, where $0 \leq x \leq \frac{4}{3}$. The introduction of a Pr vacancy does not change the number of nearest X neighbors.

The strongest effect of v is on the electronic carrier concentration n, varying between 0 and

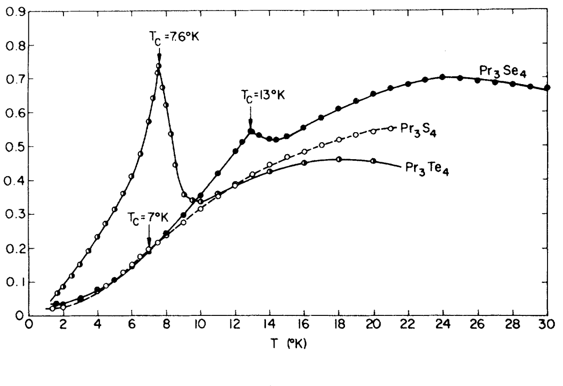

FIG. 8. Specific heat C_m/R vs temperature for Pr_3X_4 (X=S, Se, Te) between 1.4 and 30 K.

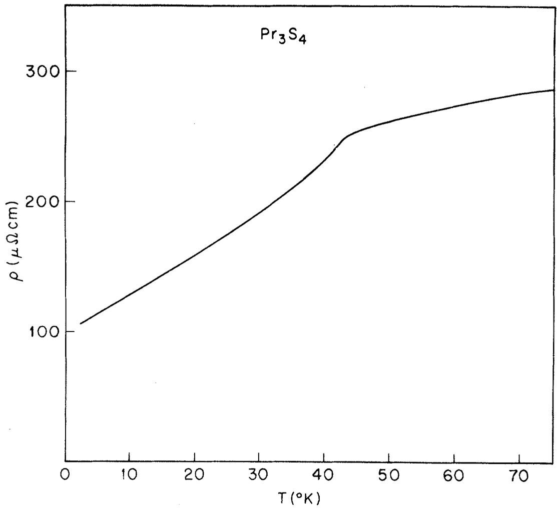

FIG. 9. Low-temperature resistivity of Pr_3S_4.

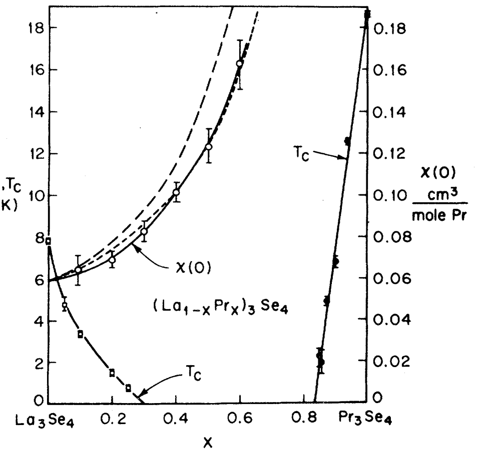

FIG. 10. Phase diagram of La_3Se_4-Pr_3Se_4.

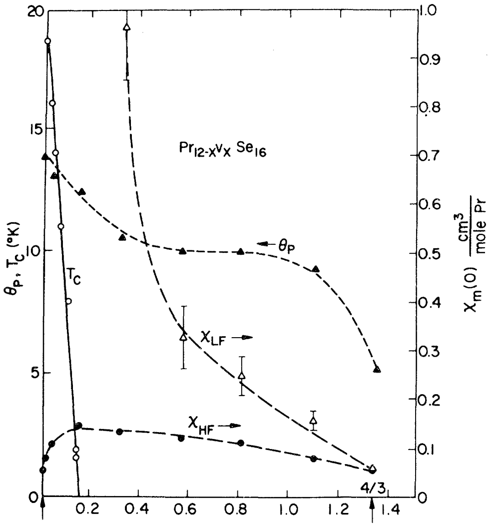

FIG. 11. Phase diagram of Pr_3Se_4-Pr_2Se_3.

$4/a^3$ (a is the lattice constant, 4 formula units per unit cell, assuming that the chalcogen elements take two electrons for the chemical bond, similar to the monochalcogenides). It is clearly seen in Fig. 11 that the exchange effects are due to the carrier concentration and that the electron carriers are responsible for the spontaneous polarization of the nonmagnetic ground state. To the extent that the crystal field is only due to the eight first X neighbors, one might be able to isolate any possible crystal-field contribution from the conduction electrons by measuring crystal-field splittings as x is varied. Although the unit cell is cubic, the point symmetry of Pr is rather low, which led us to speculate that the ninefold degeneracy of the $J=4$ ground state is probably completely lifted and that Pr_3X_4 compounds must be exchange-induced ferromagnets. However, we will not pursue here any further crystal-field considerations. (See *Note added in proof.*)

E. Pr_5Se_6

Between PrSe and Pr_3Se_4 an intermediate-phase Pr_5Se_6 has been reported by Kalitin *et al.*[63] A few samples of Pr_5Se_6 showed indeed two ferromagnetic transitions at 18.6 and 14.3 K; however, only PrSe and Pr_3Se_4 x-ray lines were present. The latter transition might be attributable to Pr_5Se_6. Unfortunately the 14.3-K transition could not be reproduced for every sample and it is conceivable that the reported Pr_5Se_6 phase is stabilized by impurities, presumably oxygen similar to the β-Pr_2S_3, which in reality was found to be a complex oxysulfide.[60] Likewise, studies on the reported La_5Se_6 showed only phases of LaSe and La_3Se_4 as far as superconductivity and x-ray analysis is concerned, in agreement with Yarembash *et al.*[64] It is interesting to note, however, that La_3Se_4 shows a resistance anomaly at 62 K, presumably related to a structural instability present in both La_3Se_4 and Pr_3Se_4. Thus, the two ferromagnetic transitions of 14.3 and 18.6 K are more likely to be related to this structural instability and not to the possible existence of a Pr_5Se_6 phase. This is further supported by the fact that stoichiometric single crystals of Pr_3Se_4 showed again two magnetic transitions of 14.3 and 17–19 K. The question of this structural instability will be studied in more detail in a forthcoming paper. (See *Note added in proof.*)

F. Tm_2X_3, Tm_5S_7, Tm_5Se_6, Tm_3Se_4

The sesquichalcogenides of the heavy rare earths differ structurally from the Pr_2X_3. δ-Tm_2S_3[15] and its cubic Tl_2O_3 phase[65] are probably Van Vleck paramagnets, as no ordering could be detected down to 0.5 K. The susceptibility levels off below about 0.9 K. This means that splitting between lowest levels is probably only a few degrees and that the low point symmetry lifts the 13-fold degeneracy completely. In contrast the black metallic Tm_5S_7 shows antiferromagnetic order near 0.6 K. Most likely it is an induced-moment system, as it is monoclinic and probably has no degenerate crystal-field levels either.

Tm_2Se_3 is again Van Vleck paramagnetic, and Tm_3Se_4 is isomorphic with Y_3Se_4 and is probably a semiconductor, its resistivity varying considerably from sample to sample between metallic conductivity and 0.1 Ω cm at room temperature, depending on stoichiometry. Tm_3Se_4 shows an effective moment of 7.32. The susceptibility levels off below 0.9 K and no magnetic ordering was detectable down to 0.45 K. Structurally, Tm_3Se_4 as well as Tm_5Se_6 are closely related to TmSe. They have a common NaCl subcell. The deep-purple Tm_5Se_6 shows antiferromagnetic order at 2.1 K, slightly above TmSe, however, with a smaller lattice constant than the mixed-valence-state compound TmSe.

Tm_2Te_3 is again Van Vleck paramagnetic, isomorphic with Tm_2Se_3.

G. Higher polychalcogenides of Pr

Now we are left with the higher polychalcogenides of Pr and Tm, among which we understand phases beyond the L_2X_3 composition, i.e., a X/L ratio larger than 1.5. They have many properties in common and we can summarize their results briefly in one sentence: All higher polychalcogenides of Pr are semiconducting Van Vleck paramagnets, perhaps with the exception of $PrTe_2$, which might be a semimetal similar to $LaTe_2$.[66]

PrS_2 is a light-brown semiconductor with a cubic unit cell containing four molecules of Pr_2S_4. Eliseev *et al.*[67] have explored structural details for the similar NdS_2 compounds as a function of sulfur concentration. NdS_2 shows a slight distortion from a cubic unit cell, not detectable in our PrS_2 Debye-Scherrer pattern. But even in this case, the Pr point symmetry is not cubic and correspondingly, the NMR spectrum showed a rather complex feature: a field-dependent linewidth and frequency, which, however, we did not analyze further.

As seen in Tables I–III the number of polychalcogenides of Pr increases from S to Te. All polyselenides are also semiconductors. If there were no bonds between S-S, Se-Se, or Te-Te, one would argue that all these compounds must be metals, like $L^{3+}X^{2-}$, where it is assumed that we have one conduction electron per formula unit. Among the polychalcogenides, $PrTe_2$ showed the lowest resistivity (of the order $10^{-3}\,\Omega\,\text{cm}$), most of the others being up to several orders of magnitude higher. Magnetically, these compounds are not very interesting and they are probably not very suitable for hyperfine-enhanced nuclear cooling owing to expected long spin-lattice relaxation rates (absence of conduction electrons), noncubic point symmetry, and the related strong pseudoquadrupolar effects.[68]

H. Higher polychalcogenides of Tm

$TmTe_3$ is the only polychalcogenide of Tm. Hall *et al.*[69] have demonstrated, however, that many polychalcogenides of Tm can be synthesized under high pressure and are isomorphic with their corresponding Pr compounds, stable at atmospheric pressure. We have not explored any of these high-pressure phases. We found an effective moment of only 6.0, suggesting the possibility of a mixed valence state. In the systematics of atomic volumes of all $L\,Te_3$ compounds,[15,70] $TmTe_3$ is not anomalous. It is possible that the anomalously low effective moment arises from deviations in stoichiometry. However, both $PrTe_3$ and $TmTe_3$ were prepared in the same way and $PrTe_3$ showed the correct effective moment of 3.59. $TmTe_3$ shows a weak susceptibility anomaly at 0.55 K. We are not sure whether this indicates magnetic order or whether it is simply a crystal-field effect in this highly anisotropic structure. Resistivities are relatively high, as in $PrTe_3$, but varied considerably from sample to sample. Determination of activation energies remains to be done. In this cursory review, however, we cannot discuss all these properties at the present time since we concentrated mainly on magnetic properties.

IV. SUMMARY AND CONCLUSIONS

In conclusion, we find that most of the chalcogenides explored in this paper are related to a number of physical problems of high current interest. It is hoped that further exploration of all the various structure groups will lead to an answer to a number of unresolved problems.

(i) The LaX and La_3X_4 compounds (X = S, Se, Te) are metallic superconductors showing a correlation between γ, the electronic specific heat, and T_c. The increase in γ from LaS to LaTe can simply be understood on the basis of Methfessel's band-structure model. Both superconducting structure types, in particular La_3X_4, in which Pr (and presumably other non-Kramers ions) is in a crystal-field singlet ground state would be suitable to test the prediction of Fulde *et al.* of the possibility of crystal-field spectroscopy by tunneling. La_3S_4 and La_3Se_4 exhibit a lattice instability of unknown origin.

(ii) The PrX compounds are all Van Vleck paramagnets fulfilling the point-charge model. They are potentially useful for hyperfine-enhanced nuclear adiabatic cooling, in particular PrS, which should cool down to 0.3 mK.

(iii) The analogous TmX compounds do not exhibit Van Vleck paramagnetism as expected theoretically. Instead they show a magnetic phase transition in an intermediate valence state, exhibiting interconfiguration fluctuation, as recently demonstrated by XPS. These materials are the first compounds exhibiting magnetic order with a nonintegral number of $4f$ electrons (except possibly TmTe, whose Tm^{3+} spectral intensity drops rapidly at low temperature). Crystal-field exchange properties are highly anomalous in such materials. This group of compounds presents an ideal system to test theories and ideas about behavior of ions with a nonintegral number of $4f$ electrons and has a significant ramification to the semiconductor-metal transition in such compounds.

(iv) The Pr_3X_4 compounds are exchange-induced ferromagnetic moment systems, exhibiting various values of T_c/Δ. These systems are presently the most promising compounds to use to test current models and ideas about the nature of a phase transition in such systems. The induced-moment behavior can be demonstrated from dilution series $La_{3-x}Pr_xX_4$ or Pr_3X_4-Pr_2X_3, the latter forming solid solutions involving Pr^{3+} vacancies. The conduction-electron concentration (and the exchange forces) can be varied continuously between ~ 0 (in Pr_2X_3) and a maximum in the metallic Pr_3X_4. Similar to the isomorphous La_3X_4, Pr_3S_4 and Pr_3Se_4 distort, whereas Pr_3Te_4 appears to be stable in the cubic Th_3P_4 phase down to 4.2 K.

(v) The higher chalcogenides with a chalcogen ratio $X/L \geq 1.5$ are semiconductors or possibly semimetals and Van Vleck paramagnetic (except probably $TmTe_3$, which might either be in a state of valence fluctuation or different ordered valence states). These materials might also be interesting for a further study of transport properties.

Note added in proof. La_3S_4, La_3Se_4, Pr_3S_4, and Pr_3Se_4 were found to exhibit a structural (tetragonal) phase transition (as concluded from elastic measurements) at 90, 62, 45, and 30–40 K, respectively. The two magnetic peaks in Pr_3Se_4 may therefore be related to magnetic order of inequivalent sites. [See E. Bucher, P. D. Dernier, J. P. Maita, L. D. Longinotti, B. Luthi, and P. S. Wang, in Annual Conference on Magnetism and Magnetic Materials, San Francisco, Calif., 1974 (unpublished)].

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