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Electrical Transport and Magnetic Properties of Misfit Layered Compounds Intercalated with Cobaltocene

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The electrical and magnetic properties of misfit layered cobaltocene complexes of composition $(PbS)_{1.18}(TiS_2)_2(CoCp_2)_{0.28}$, $(PbS)_{1.14}(TaS_2)_2(CoCp_2)_{0.28}$, and $(PbSe)_{1.12}(NbSe_2)_2(CoCp_2)_{0.27}$ [$Cp = C_5H_5^-$] were investigated. All the pristine chalcogenides studied exhibit a metallic behavior and a magnetic susceptibility virtually independent of temperature. Moreover, the Ta and Nb compounds—the later impurified with $NbSe_2$—undergo a superconducting transition at low temperatures ($T_C < 4$ K). Upon cobaltocene intercalation, the Ta and Nb systems behave similarly. The superconducting transition temperature changes very little and the metallic behavior is preserved: the susceptibility is temperature-independent, whereas the resistivity increases with increasing temperature. This is consistent with an electron transfer from the metallocene to the host. The Ti intercalate behaves markedly differently. Thus, the complex undergoes a metal semiconducting transition below 70 K, and the magnetic data are significantly temperature-dependent. This localized moment may be consistent with the minimum observed in the resistivity values. The good overlapping properties 4d and 5d orbitals relative to 3d orbitals may account for the delocalization of the electron donated by the guest to the conduction band of the host.

Introduction

Ternary chalcogenides of $(MX)_{1+x}(TX_2)_2$ stoichiometry (with M = Sn, Pb, Bi, or lanthanides and T = Ti, Nb, Ta; X = S, Se; $0.12 \le x \le 0.19$) make up a new class of composite layered chalcogenides that has received special attention during this decade because of their peculiar structures and physical properties.[1] Their structures, well-documented for $(PbS)_{1.14}(NbS_2)_2$,[2] $(PbS)_{1.18}(TiS_2)_2$,[3] and $(PbSe)_{1.12}(NbSe_2)_2$[4] from X-ray single-crystal measurements, consist of two successive TS_2 sandwiches alternating with an MX double layer ($-MX-TX_2-TX_2-MX-TX_2-TX_2-$) stacked along the *c* axis. Alternatively, in terms of such stacking, these compounds can be formally described as two-stage intercalation compounds of the transition metal disulfide, TX_2. The atomic arrangement of MX layers is based on a rock-salt structure and the TX_2 units are geometrically identical with the layers found in the binary TX_2 layered compounds. The unit cell axis of both sublattices, MX and TX_2, are identical in the *b* direction and incommensurate in the *a* direction. This introduces a certain degree of nonstoichiometry, *x*, which can be determined from the a_{TX_2}/a_{MX} ratio.

Slab stacking in MX and TX_2 results in the formation of empty van der Waals gaps at the TX_2/TX_2 interfaces that can be occupied by different guest species. This property has attracted our interest in the past few years, during which we have successfully intercalated atomic and molecular guest species under mild experimental conditions (soft chemistry methods).[5] Recently, by direct synthesis from the elements at high temperatures,

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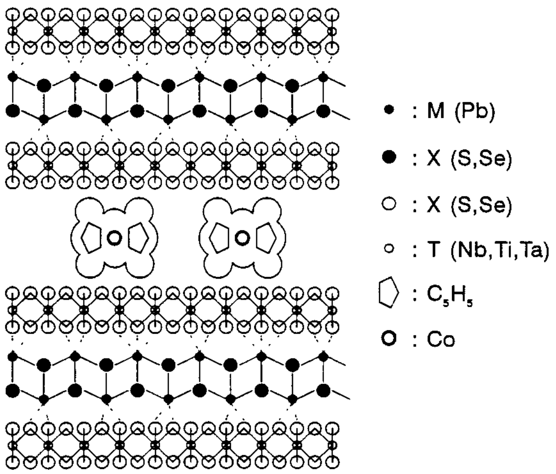

Figure 1. Idealized projection along [010] of a misfit layered compound containing paired TX_2 sandwiches intercalated with cobaltocene.

Ohno[6] prepared the intercalates $Cu_y(MS)_{1+x}(NbS_2)_2$ (M = Ce, Sm) and Suzaku et al.,[7] $E_y(MS)_{1+x}(TiS_2)_2$ (E = Fe, Ni; M = La, Ce).

Cobaltocene is among the molecular species that can be accommodated in the unoccupied van der Waals gaps, simply by direct reaction between the organometallic compound in acetonitrile and the chalcogenide.[8] Such an intercalation was first reported for the semiconducting phases SnS_2, $SnSe_2$,[9] ZrS_2, $ZrSe_2$, and ZrSSe[10] and for some transition metal dichalcogenides.[11] The intercalation leads to a $TX_2(CoCp_2)_{0.25-0.30}$ composition which corresponds to complete filling of the space in the van der Waals gap between the sandwiches. On the basis of magnetic properties and photoelectron spectroscopy, the degree of oxidation of $CoCp_2$ to $CoCp_2^+$ can be determined. Oxidation is complete for $SnS_2\,(CoCp_2)_{0.31}$ but only partial for ZrX_2 intercalates.[10] For misfit layered compounds with two successive TX_2 sandwiches, the structural model for $CoCp_2$ intercalates derived from X-ray powder and electron diffraction data is consistent with a cobaltocene molecule present at every TX_2/TX_2 interface; on the other hand, MX/TX_2 interfaces remain empty[8] (see Figure 1). Moreover, X-ray photoelectron spectroscopy revealed the occurrence of significant charge transfer from the guest to the host, with formation of roughly 80% cobaltocinium ion. The intercalation of cobaltocene has no effect on the core-binding energies of the host matrix elements.

With the aim of obtaining a deeper knowledge of the electronic structure of these novel intercalates, in this work we studied the transport and magnetic properties of some with a view to gaining substantial insight in to the electronic changes in the host induced by the guest molecules.

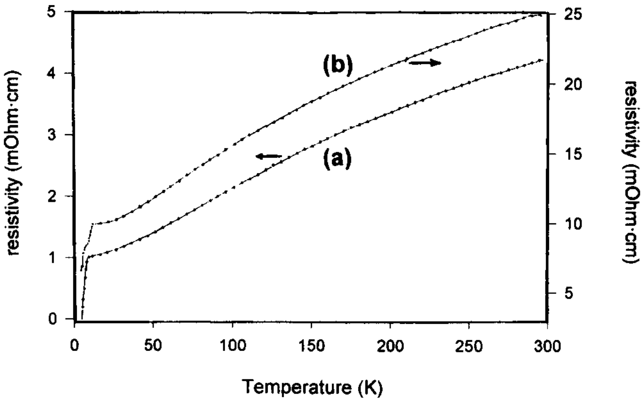

Figure 2. Temperature dependence of resistivity for (a) $(PbSe)_{1.12}(NbSe_2)_2$ and (b) $(PbSe)_{1.12}(NbSe_2)_2(CoCp_2)_{0.27}$.

Experimental Section

Misfit layered compounds of Ti, Nb, and Ta, $(PbS)_{1.18}(TiS_2)_2$, $(PbSe)_{1.12}(NbSe_2)_2$, and $(PbS)_{1.14}(TaS_2)_2$ were prepared by heating mixtures of the corresponding elements (supplied by Strem Chem.) in appropriate amounts in evacuated silica tubes. Further details concerning the heating steps and temperatures used are given elsewhere.[8] The compounds were obtained as small platelike crystals with metallic luster and were manually ground in an agate mortar.

Cobaltocene intercalates were prepared by immersing the crystalline host in a solution of $CoCp_2$ in dry acetonitrile (Strem Chem.). About 100 mg of the Ti compound and ~200 mg of the other two chalcogenides were mixed with 2 mL of 0.05 M cobaltocene solution with the aim of obtaining a guest/host molar ratio greater than 0.3, the value found in previous work.[8] The suspensions were placed in sealed Pyrex tubes, previously frozen under liquid nitrogen and evacuated to $P < 10^{-3}$ mbar. A heating period of two weeks at 60 °C was long enough to achieve 100% conversion. At the end of the reaction, each tube was opened in a drybox, the suspension was filtered and the solid was washed with acetonitrile. The intercalates were then stored in sealed glass tubes under N_2 until their characterization. The amount of intercalated cobalt was measured by atomic absorption spectroscopy and the stoichiometry confirmed by elemental analysis. The intercalate compositions obtained were $(PbS)_{1.18}(TiS_2)_2(CoCp_2)_{0.28}$, $(PbS)_{1.14}(TaS_2)_2(CoCp_2)_{0.28}$, and $(PbSe)_{1.12}(NbSe_2)_2(CoCp_2)_{0.27}$. Further details of their characterization can be found elsewhere.[8]

Electrical resistivity measurements on compacts were performed by using a Model 6000 Physical Property Measurement System (Quantum Design), equipped with LR700 AC resistance bridge and a Model 720S eight sensor multiplexer from Linear Research, Inc. The samples were pressed at 1 ton into cylinders 6 mm in diameter and about 1 mm in thickness. The van der Pauw method was used. Magnetic susceptibility was measured by using a commercially available SQUID magnetometer over the temperature range 1.7−300 K under an applied magnetic field ranging from 0.5 to 5 kOe.

Results and Discussion

Electrical Conductivity Measurements. Figures 2 and 3 show the temperature dependence of the resistivity for the Nb and Ta chalcogenides and their cobaltocene intercalates. Between 30 and 300 K the resistivity of the four compounds increases with increasing temperature, which is indicative of metallic behavior. The resistivity values obtained at 10 and 300 K are given in Table 1. The resistivity for the pristine Nb chalcogenide at room temperature is nearly 1 order of magnitude greater than that in the *a*−*b* plane measured by Auriel et al.[4] on single crystals. Below 5 K, the resistivity drops to zero, which suggests a metal super-

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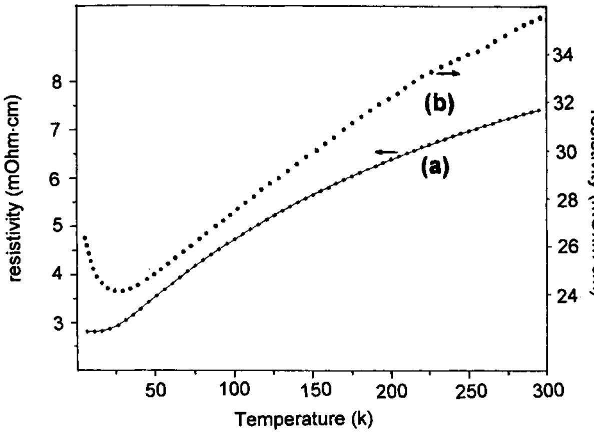

Figure 3. Temperature dependence of the resistivity for (a) $(PbS)_{1.14}(TaS_2)_2$ and (b) $(PbS)_{1.14}(TaS_2)_2(CoCp_2)_{0.28}$.

Table 1. Resistivity of the Nb and Ta Misfit Layered Chalcogenides and Their Cobaltocene Intercalates

compound	ρ (10^{-5} Ω.m) 10 K	300 K
$(PbSe)_{1.12}(NbSe_2)_2$	1.2	4.3
$(PbSe)_{1.12}(NbSe_2)_2(CoCp_2)_{0.27}$	10.0	25.0
$(PbS)_{1.14}(TaS_2)_2$	2.8	7.2
$(PbS)_{1.14}(TaS_2)_2(CoCp_2)_{0.28}$	26.5	35.5
$(PbSe)_{1.12}(NbSe_2)_2$[4]	–	0.5
$(PbS)_{1.13}TaS_2$[13]	0.01	0.16

conducting transition. This finding is consistent with resistivity data measured on single crystals,[4] which exhibited a superconducting state with T_c at 2.9 K. However, our data warrant two comments. First, the superconducting transition is broader (~2.8 K) than that reported by Auriel et al.[4] (<2 K). Nader et al.[12] recently reinvestigated superconductivity in $(PbSe)_{1.12}(NbSe_2)_2$ and found the superconducting transition to have a T_C of 2.9 K and a width of only 0.12 K. Second, the T_C measured is above 4 K and hence somewhat higher than those found by the above-mentioned authors. In this context, it is worth noting that $NbSe_2$ behaves as superconductor with $T_C \approx 7$ K. For this reason, the purity of the $(PbSe)_{1.12}(NbSe_2)_2$ compound was examined by recording its XRD pattern using a Guinier camera where the effect of the preferred orientation of particles in the sample holder was just the opposite to that in the standard powder diffractometer. We can thus conclude that $NbSe_2$ is present as an impurity. This may account for the relatively broad metal superconducting transition in this metal layered chalcogenide. The resistivity values for $(PbS)_{1.14}(TaS_2)_2$ are also greater than that reported for the in-plane resistivity in $(PbS)_{1.13}$ TaS_2 single crystals,[13] probably because of the high anisotropy normal to and along the *c* axis. No sign of a superconducting transition was observed over the temperature range used in these measurements (4–300 K). At lower temperatures, however, the compound behaves as superconductor (see below).

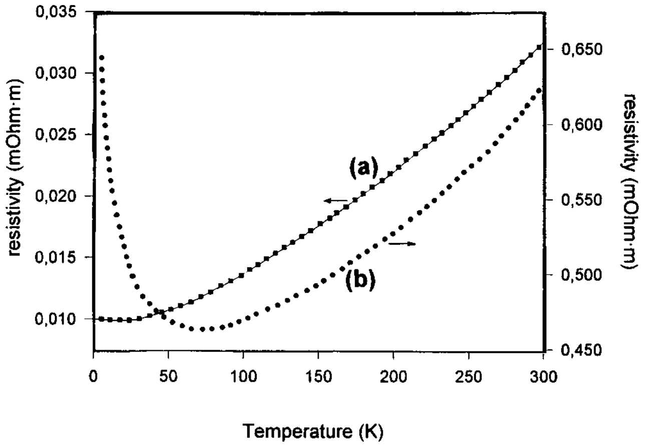

Figure 4. Temperature dependence of the resistivity for (a) $(PbS)_{1.18}(TiS_2)_2$ and (b) $(PbS)_{1.18}(TiS_2)_2(CoCp_2)_{0.28}$.

The intercalation of cobaltocene in these two chalcogenides induces appreciable changes in resistivity. Thus, at room temperature, the resistivity is increased by a factor about 5. Also, the resistivity ratio, defined as ρ_{300K}/ρ_{10K}, decreases by a factor about 1.8 (see Table 1). However, our data contrast with those previously found for $SnS_2(CoCp_2)_{0.31}$,[9] $SnSe_2(CoCp_2)_{0.33}$,[9] and $ZrS_2(CoCp_2)_{0.28}$,[10] the resistivities of which are lower than those of the pristine compounds because these are semiconductors, not metals as in our case. At low temperatures, the Nb system maintains its superconductor behavior; however, the resistance drop begins at somewhat higher temperature (near 7 K). Moreover, a shoulder is observed at about 4 K. These results provide evidence of the multiphase nature of this system. The X-ray Guinier pattern is consistent with the presence of two phases of basal spacing 12.33 and 11.80 Å, respectively. The former can be assigned to $NbSe_2(CoCp_2)_x$[11] and the second to $(PbSe)_{1.12}(NbSe_2)_2(CoCp_2)_x$. The abrupt resistivity drop observed at about 4 K must correspond to this latter phase and reveals the little influence of the intercalation process on T_C. This is coincident with the magnetic measurements, as shown in the next section. No superconducting behavior was observed for the Ta intercalate over the temperature range studied either. Rather, the resistivity of this complex was found to increase slightly below 30 K. As discussed below, the origin of this phenomenon could be the small Curie–Weiss component found.

Figure 4 shows the temperature dependence of resistivity for the pristine and intercalated Ti compounds. In contrast with the electrical properties found for the Nb and Ta systems, the metallic type of conduction in the Ti original compound is substantially altered upon cobaltocene intercalation; in addition, the resistivity values measured between 4 and 300 K are even more markedly increased. This latter fact is consistent with data recently reported by Suzuki et al.[7] for the intercalates $Ni_{0.46}(CeS)_{1.19}(TiS_2)_2$ and $Fe_{0.33}(CeS)_{1.19}(TiS_2)_2$, the resistivity of which also exceeds that of the pristine compound. One salient finding is the differential temperature dependence of the intercalate resistivity (see Figure 4) relative to the host compound. Thus, below about 100 K, an upturn in resistivity is observed. A resistivity minimum at low temperatures (the Kondo effect) is known to occur in alloys. In fact, this behavior has been associated to additional scattering of electrons by the magnetic moments of the solutes.[14] This resistivity anomaly was recently found in the intercalate $Fe_{0.33}$-

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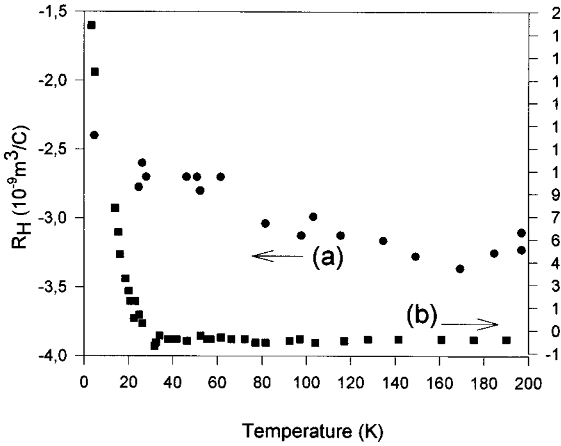

Figure 5. Temperature dependence of the Hall coefficient, R_H, for (a) $(PbS)_{1.18}(TiS_2)_2$ and (b) $(PbS)_{1.18}(TiS_2)(CoCp_2)_{0.28}$.

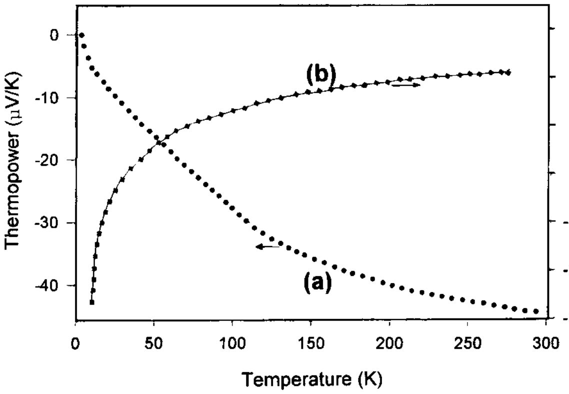

Figure 6. Temperature dependence of the Seebeck coefficient, *S*, for (a) $(PbS)_{1.18}(TiS_2)_2$ and (b) $(PbS)_{1.18}(TiS_2)_2(CoCp_2)_{0.28}$.

Table 2. Transport Properties of $(PbS)_{1.18}(TiS_2)_2$ and $(PbS)_{1.18}(TiS_2)_2(CoCp_2)_{0.28}$

	ρ (10^{-6} Ωm)		R_H (10^{-9} m^3 C^{-1})		*z* (e$^-$/Ti)	α (μV K^{-1})
compound	4 K	300 K	4 K	300 K	4 K	300 K
$(PbS)_{1.18}(TiS_2)_2$	10	33	−2.7	−3.4	0.20	−40
$(PbS)_{1.18}(TiS_2)_2(CoCp_2)_{0.28}$	650	630	200	−7	-	22
$(PbS)_{1.18}(TiS_2)_2$[15]	1.1	2.7	−2.7	−3.0	0.20	−60

$(CeS)_{1.19}(TiS_2)_2$.[7] However, the absence of the Kondo effect in incommensurate misfit layered compounds and M_xTiS_2 was used by Suzuki et al.[7] to discard the magnetic moments in $E_x(MS)_y(TiS_2)_2$ as the origin of the resistivity minimum. Instead, the −ln *T* dependence of ρ was assigned to a weak carrier localization caused by the lattice incommensuration on the electronic structure. We believe our results can be better explained in terms by the local magnetic moment of the compound, as discussed in the next section.

A complementary characterization of the electrical properties of the Ti system was undertaken by examining the Hall and Seebeck coefficients starting from 4 K. The temperature dependence of these coefficients is illustrated in Figures 5 and 6, respectively. The electrical transport properties of both compounds are summarized in Table 2. The metallic behavior of the original compound is quite consistent with the data reported by Auriel et al.,[15] albeit with some differences in the transport parameters. Thus, the resistivity is about 10 times higher, and the Seebeck coefficient, *S*, at 300 K is less negative. Conduction is due to electrons in a slightly occupied Ti 3d t_{2g} conduction band of the TiS_2 sandwiches (0.2 e/Ti). The electron concentration is lower than that calculated by Kondo et al.[16] for $(CeS)_{1.16}(TiS_2)_2$, (0.51 e/Ti). This is consistent with the widely accepted fact that electron donation from MX to TX_2 is more substantial when M is a lanthanide rather than Pb or Sn.

The complex temperature dependence of the resistivity of the Ti intercalate is also reflected in its Hall and Seebeck coefficients (see Figures 5 and 6, and Table 2). The Hall coefficient, R_H, is positive below 25 K and as high as 200×10^{-9} cm^3 C^{-1} at 4 K; also it decreases abruptly as the temperature is raised. At about 25 K, the coefficient becomes negative and changes little with temperature. These results suggest that electrons and holes play a significant role in the conducting properties of the intercalate. The thermoelectric power, *S*, of the intercalate also behaves very differently from that of the pristine compound. There is a sign change at ~25 K; also, in the negative region, *S* decreases strongly with decreasing temperature, consistent with a semiconducting behavior (at 4 K, $S = -22$ μV K^{-1}). At low temperatures, the positive sign of R_H and the negative sign of *S* indicate the presence of light holes and heavy electrons; at room temperature, light electrons and heavy holes are present. These results are rather different from those which one would expect from the donation of an electron from $CoCp_2$ to the 3d t_{2g} conduction band of the host. The partial occupancy of the t_{2g} band by the electrons transferred from the guest should favor the metallic behavior of the host.

Magnetic Susceptibility Measurements. The temperature dependence of the molar magnetic susceptibility (χ) for the three misfit layered chalcogenides and their cobaltocene intercalates, as corrected for the intrinsic diamagnetism of the constituent atoms, are shown in Figures 7a,b and 8. Table 3 gives the χ values for the compounds studied at 10 and 300 K. All the pristine compounds exhibit a virtually temperature-independent susceptibility above 10 K, in agreement with the above-described metallic behavior. Moreover, Curie tails are hardly perceptible, which suggests the absence of significant amounts of paramagnetic impurities in the starting compounds. The susceptibility of $(PbS)_{1.19}(TiS_2)_2$ is somewhat greater than that of TiS_2,[17] whereas that of $(PbS)_{1.14}(TaS_2)_2$ is similar to the susceptibility reported for the monolayer compound $(PbS)_{1.13}TaS_2$.[13] A marked decrease in χ below 4 K is observed for the Ta compound, suggestive of a superconducting behavior with $T_C \approx 3.3$ K (see Figure 7b). The compound $(PbS)_{1.13}TaS_2$ also behaves as a low-temperature superconductor, with T_C from 3.07 to 3.11 K,[1] which are close to the value for the bilayer compound. Thus, the differential stacking sequence of the layers barely affects the metal superconducting temperature transition.

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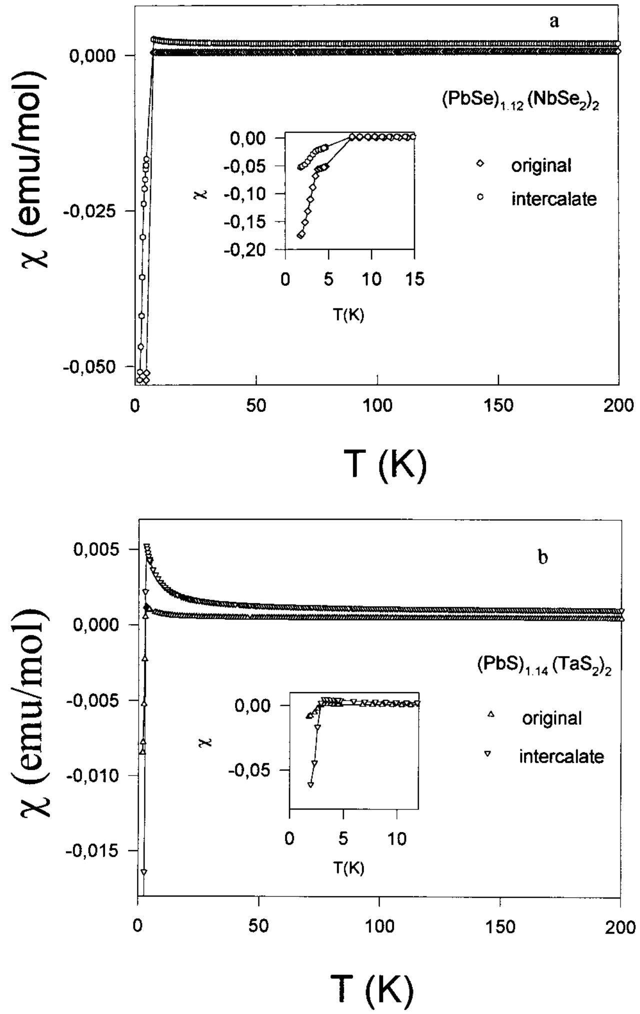

Figure 7. Temperature dependence of the magnetic susceptibility of Nb (a) and Ta (b) misfit layered compounds and their intercalates with cobaltocene. The insets show susceptibility changes in the low-temperature region.

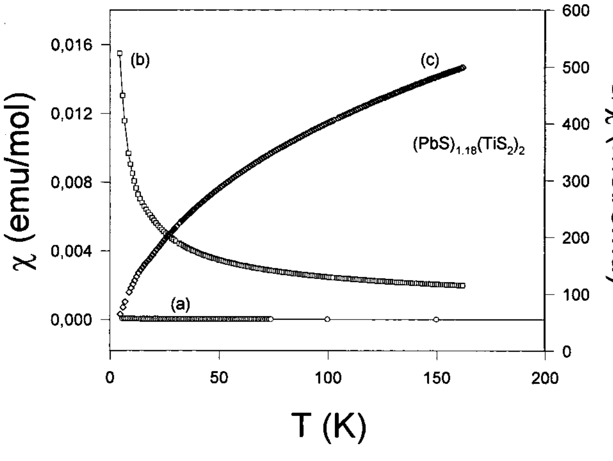

Figure 8. Temperature dependence of the magnetic susceptibility of the Ti misfit layer sulfide (a) and its intercalate with cobaltocene (b). χ^{-1} for the Ti intercalate is also plotted (c).

Table 3. Magnetic Susceptibility of (PbS)$_{1.18}$(TiS$_2$)$_2$, (PbS)$_{1.14}$(TaS$_2$)$_2$, and (PbS)$_{1.12}$(NbSe$_2$)$_2$ and of Their Intercalates with Cobaltocene (emu/mol)

compound	10 K	300 K
(PbS)$_{1.18}$(TiS$_2$)$_2$	0.6×10^{-4}	1.9×10^{-5}
(PbS)$_{1.18}$(TiS$_2$)$_2$(CoCp$_2$)$_{0.28}$	8.5×10^{-3}	20×10^{-3}
(PbS)$_{1.14}$(TaS$_2$)$_2$	7.0×10^{-4}	4.4×10^{-4}
(PbS)$_{1.14}$(TaS$_2$)$_2$(CoCp$_2$)$_{0.28}$	2.6×10^{-3}	9.8×10^{-4}
(PbS)$_{1.12}$(NbSe$_2$)$_2$	2.2×10^{-4}	2.2×10^{-4}
(PbS)$_{1.12}$(NbSe$_2$)$_2$(CoCp$_2$)$_{0.27}$	2.3×10^{-4}	2.3×10^{-4}

A dramatic decrease in χ below 7 K is also observed in the Nb compound and its intercalate (see Figure 7 a). As can be seen in the inset of the figure, the susceptibility drop occurs in two steps for both compounds, the lower temperature being centered at about 3 K. These results are consistent with the resistivity results; their origin must be the presence of NbSe$_2$ as an impurity. The T_C at 3 K should be assigned to the ternary chalcogenide and, as in the Ta system, changes little upon cobaltocene intercalation.

The susceptibility of the Ta and Nb intercalates, Figure 7, is also essentially independent of temperature and changes little upon intercalation. This behavior resembles that of the TaS$_2$ (CoCp$_2$)$_{0.25}$ intercalate, the susceptibility of which is independent of temperature down to 2 K.[18] By taking into account that the magnetic moments of CoCp$_2$ and CoCp$_2^+$ are 1.81 and 0 μB, respectively, the loss of local moment is consistent with the transfer of one electron from the molecule to the host; this agrees with the XPS results,[8] which suggest that most of the cobaltocene molecules undergo rapid oxidation to CoCp$_2^+$ while electrons are transferred to the conduction band of the chalcogenide. Band structure calculations[19,20] for (MS)$_{1+x}$TS$_2$ (M = Sn, Pb; T = Nb, Ta) have shown that the states just below the Fermi level correspond to Nb 4 d$_{z^2}$ states (Ta 5 d$_{z^2}$ states). These bands should be more than half-filled owing to the small extent to which charge is transferred from MX layers to TX$_2$ layers. This means that the electron donation from the guest to the host should decrease the density of states at the Fermi energy, $N(E_F)$, thus decreasing the magnetic susceptibility [$\chi = \mu_B{}^2 N(E_F)$]. Apparently, the susceptibility calculated χ (see Table 3) deviates from this behavior, probably because of the presence of a small amount of the guest as Co^{2+} species. In fact, the magnetic susceptibility data for the Ta intercalate below 30 K exhibit a small component of Curie−Weiss paramagnetism probably due to localized electrons. This may account for the small increase in resistivity below 30 K observed in this intercalate (see Figure 3).

A dramatic change in magnetic properties occurs when cobaltocene is intercalated into the Ti compound (see Figure 8). In addition to the significantly increased susceptibility, the temperature-dependent component dominates at temperatures below 100 K, where the resistivity minimum begins to appear. On the other hand, as can be seen from Figure 8, the (PbS)$_{1.19}$(TiS$_2$)$_2$(CoCp$_2$)$_{0.28}$ intercalate does not obey the simple Curie−Weiss law. This behavior contradicts that of other metallocene intercalates [e.g., SnS$_2$(CoCp$_2$)$_{0.30}$,[9] TaS$_2$(CrCp$_2$)$_{0.28}$,[18] and ZrS$_2$(CrCp$_2$)$_{0.2}$[10]]. The Curie−Weiss expression for these compounds was accurately fitted over a wide temperature range (from 4 to 300 K). The magnetic moment of pure CoCp$_2$ is temperature-de-

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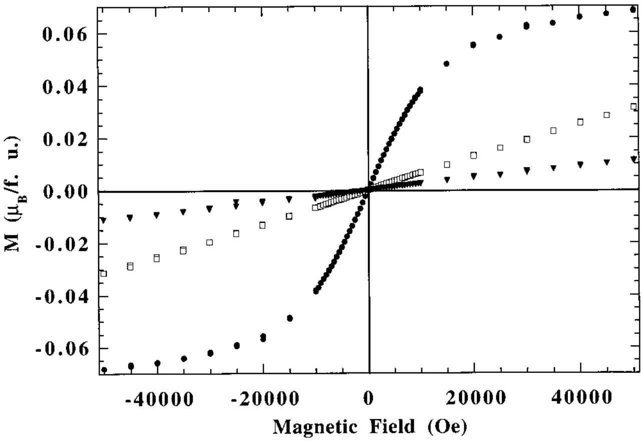

Figure 9. Magnetization curves for the Ti intercalate recorded at different temperatures: (▽) 100 K; (□) 25 K; and (●) 2 K.

pendent; over the temperature range 1−20 K, the magnetic moment is 1.45 μB and the Curie constant 0.263 (emu K)/mol.[21] At 160 K, the magnetic moment of $CoCp_2$ is 1.73 μB and the Curie constant 0.374 (emu K)/mol. If cobaltocene is assumed to be intercalated as neutral molecule, then the calculated Curie constant should be $0.374 \times 0.28 = 0.104$ (emu K)/mol. The magnetic susceptibility at 160 K should thus be $C/160 = 0.00065$ emu/mol. The measured χ at 160 K, however, is larger, (viz., 0.0020 emu/mol.) We believe that the difference, $0.0020 - 0.00065 = 0.00135$ emu/mol at 160 K, is due to some impurity probably formed by decomposition of some $CoCp_2$.

To acquire further knowledge on the magnetic behavior of the Ti intercalate, isothermal magnetic curves were also measured up to 100 K at different temperatures. The results are shown in Figure 9. At 25 and 100 K, magnetization increases linearly with field, however, at 2 K, it increases abruptly at low fields and at high fields it tends to saturation. Magnetization almost saturates at 40 kOe, reaching a value of 0.048 μB (a low saturation magnetization moment, indeed). One other significant finding is that the apparent magnetization is zero when no external field is applied. This latter behavior is typical of superparamagnetic materials, for which size reduction in single-domain particles eventually causes coercivity to fall.[22] The nature of this phase with this magnetic ordering is unknown at present. If we tentatively assume the formation of cobalt to originate from the decomposition of $CoCp_2$, then, taking into account that the saturation moment of this metal is 1.715 μB, the calculated proportion of cobalt should be less than 0.8%. Moreover, the absence of hysteresis and the low-temperature magnetic ordering may be qualitatively justified by considering a model including ferromagnetic clusters,[23] resembling a superparamagnetic assembly of atoms. In fact, particle size is sufficient to dramatically alter the hysteresis curves.[24]

Data corrected for the contribution of this impurity lead to a roughly linear $1/\chi$ vs T plot with a Curie constant of 0.112 (emu K)/mol, which is close to that expected for unoxidized $CoCp_2$ in the lattice. The local magnetic moment thus derived may account for the minimum in the resistivity vs T plot. However, there is some contradiction between magnetic properties which suggests that the intercalation of cobaltocene involves neutral molecules and XPS results that reveal the presence of a significant amount of cobaltocinium ions ($CoCp_2^+$). In any case, the chemical similarities between the intercalation behavior of Nb and Ta systems and their differences from the Ti system can be explained by taking into account the good overlapping properties of the 4d and 5d orbitals relative to 3d orbitals. This facilitates charge transfer from the cobaltocene molecule so the donated electron is delocalized in the conduction band of the host. Thus, the intercalate behaves as a typical metal with a weak, temperature-independent paramagnetism associated with metallic electrons. Further experimental work will be required to trace the origin of the Curie term and make it compatible with the localization of the electrons donated to $(PbS)_{1.18}(TiS_2)_2$ by the metallocene.

Conclusions

The electrical transport and magnetic properties of the cobaltocene intercalates of misfit layered chalcogenides $(PbS)_{1+x}(TS_2)_2$ (T = Ti, Ta) and $(PbSe)_{1.12}(NbSe_2)_2$ with two successive TX_2 sandwiches were investigated. The cobaltocene molecule is ionized in the Nb and Ta intercalates and the superconducting transition temperature observed for the hosts changes little upon intercalation. The Ti intercalate behaves differently: its magnetic properties suggest the presence of un-ionized $CoCp_2$ in addition to an impurity that exhibits superparamagnetic behavior below 25 K. The electrical transport properties are rather different from those of the pristine compound; also, localization of the charge carriers is observed at low temperatures.

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