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Role of Vacancies in Misfit Layered Compounds: The Case of the Gadolinium Chromium Sulfide Compound

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The misfit layer compound $(GdS)_{1.27}CrS_2$ has been found to be nonstoichiometric. The nonstoichiometry is caused by gadolinium vacancies which were detected by a careful microprobe chemical analysis. This layered composite phase is built by alternate stacking of [GdS] and $[CrS_2]$ layers along the $\vec{c}$ axis. The different sublattices ([GdS] and $[CrS_2]$) both have an orthorhombic symmetry. The b parameters (b_1 and b_2) and c parameters (c_1 and c_2) of both subsystems are identical whereas the two a parameters have different values ($a_1 = 5.454(1)$ Å and $a_2 = 3.451(1)$ Å). The a_1/a_2 ratio is irrational and determines the incommensurate character of this compound. The complete X-ray structure determination has already been published. Therefore, only the studies of the [GdS] sublattice ($a_1 = 5.454(1)$ Å, $b_1 = 5.8098(6)$ Å, $c_1 = 21.461(4)$ Å; space group *Cmca*; $Z = 8$; $R = 0.054$) and of the projection of the complete structure onto the (b,c) plane (space group: *Cmca*; $R = 0.058$) were redone in context with the new results. The results of the chemical analysis were confirmed by this study. The exact chemical formula of the compound is therefore $(Gd_{1.16}\square_{0.11}S_{1.27})CrS_2$. Including the vacancies in the composition leads to an almost exact charge balance between Gd^{3+}, Cr^{3+}, and S^{2-} ($1.16 \times Gd^{3+} + Cr^{3+} = 6.48$; $3.27 \times S^{2-} = 6.54$). The electronic transfer from the [GdS] to the $[CrS_2]$ layer is such that no excess electrons exist. Magnetic and electrical transport measurements on single crystals are discussed, and for the first time, the semiconducting behavior of this class of compounds can be explained. The present results can also help to understand the discrepancies observed in the $(LnS)_xVS_2$ series.

Introduction

In the misfit layered compounds $(MS)_xTS_2$, often abbreviated as "MTS_3", two layered sublattices alternate along a common axis, labeled as $\vec{c}$ axis (Figure 1a). One layer has the composition TS_2, in which the transition metal atoms, T, are either octahedrally coordinated (when T = Ti, V, or Cr) or trigonally prismatically coordinated (when T = Ta or Nb) by S atoms. The other layer, previously thought to have the composition MS, consists of two layers forming a distorted NaCl structure parallel to the (100) plane (Figure 1b). M is usually a post-transition main group or a rare earth metal, such as Sn, Bi, Pb, La, or Gd. In this paper we show that the [MS] layer can support a large number of cation vacancies and that knowledge about these defects can help to explain physical properties.

In the misfit compounds the periodicity $\vec{c}$ characterizes the layer stacking. In the plane of the layer each sublattice is characterized by two lattice parameters, a and b. So far it has always been found that the $\vec{b}$ axes of the two sublattices are identical, but the $\vec{a}$ axes are different: a_1 for the [MS] layer and a_2 for the $[TS_2]$ layer. In general the two $\vec{a}$ axes are incommensurate, so that na_1 is not equal to ma_2 for any small value of the integers n and m. This incommensurability is reflected in the more accurate chemical formula $(MS)_xTS_2$, where x ranges from 1.08 to 1.28 for compounds studied so far. The theoretical value for x is easily determined from the lattice parameters. The unit cells of the [MS] and $[TS_2]$ substructures contain four and two chemical formula units, respectively. Thus in a crystal the ratio of [MS] units to $[TS_2]$ units is given by $2V_2/V_1$, where V_1 and V_2 are the volumes of the [MS] and $[TS_2]$ subcells, respectively. In most cases the symmetry of the subcells is orthorhombic or monoclinic and the projection of the $\vec{c}$ axis normal to the plane defined by $\vec{a}$ and $\vec{b}$ must be the same for both subcells, so that $x = 2a_2/a_1$.[1]

Except for "$LaCrS_3$", according to Kato *et al.*,[2] the [MS] layer has been assumed to be stoichiometric in all the compounds that have been studied so far. We have, however, noted in certain previously reported structure refinements that the value of x was less than the theoretical value. For example, for $(GdS)_xCrS_2$, the theoretical value of x is 1.27 but the refined value that best matches the observed diffraction intensities is 1.17.[3] Similar discrepancies were observed for $(YS)_xCrS_2$.[4] At the time, this much lower [MS] "content" was assumed to be related to either stacking faults in the [MS] and/or $[TS_2]$ sublattices or being the consequence of the mutual modulation of the sublattices. This modulation is strongest for atoms at the interface of the two layers. Following this reasoning, the [MS] layer is always strongly modulated and in this layer the M atoms, which are located on the exterior of the layer, are modulated the strongest. However, in other cases, when T = Ti, Nb, or Ta, the difference between the calculated and refined value is smaller, often within the expected errors of the refined values.

Many measurements of the physical properties of these phases have been reported but their interpretation has proved to be difficult.[1,5-7] For example, the phases $(LnS)_xCrS_2$, where Ln = rare earth, are semiconductors and magnetic measurements show that the Cr^{3+} moment is identical to the expected free ion value (this is especially clear when Ln = La and the Cr moment is the only one present). A valence electron count would then be consistent with Ln^{3+}, Cr^{3+}, and S^{2-}, with $x - 1$ electrons remaining. These "excess" electrons should result in metallic conductivity, in contrast to the observed semiconducting behavior.[8] Similarly, the $(LnS)_xVS_2$ compounds are reported to be semiconducting[9,10]

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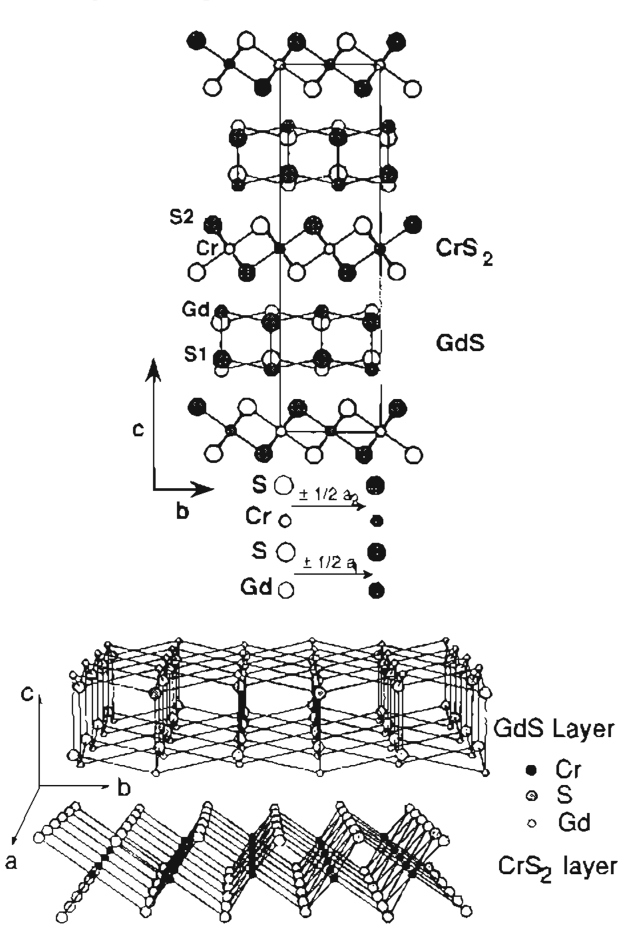

Figure 1. (a) Top: Projection of the complete structure of "$GdCrS_3$" along the misfit [100] axes. (b) Bottom: Perspective view of the [GdS] and the [CrS_2] layers.

(except in the case of Ln = Sm, where both a metallic and semiconducting phase have been reported), while the compound $LiVS_2$ is metallic.[11] In both cases about one electron should be transferred to the VS_2 layer and the electrical properties should be similar, in contrast to the reported data.

In order to discover the root of these discrepancies, we have undertaken a detailed chemical analysis of the composition of single crystals of several misfit compounds. The results are permitting us to propose a vacancy model which allows a coherent explanation of the previous data. These results have important implications for the understanding of the stability of these phases and are considered in the discussion.

Chemical Analysis

Analyses were performed at the BRGM-CNRS common laboratory (Orléans, France), using a Cameca SX 50 electron microprobe. Synthetic samples were mounted using a cold-setting epoxy (araldite), and prior to analysis, polished sections were observed under a reflected-light polarizing microscope. The width of tabular single crystals varies from 50 μm to 2 mm, and their thickness from 10 to 100 μm; twinning parallel to (001) is often observed.

The operating conditions for microprobe analysis were as follows: accelerating voltage 20 kV, beam current 20 nA. Standards used were (element, X-ray emission line, counting time) as follows: Cr metal (Cr Kα, 10 s); FeS_2 (S Kα, 10 s); (La, Ce, Pr, Al)-oxide (La Lα, 20s); Y_2O_3 (Y Lα, 20 s); (Gd, Eu, Tb, Al)-oxide (Gd Lα, 20 s). Since the main results discussed here concern the "$GdCrS_3$" compound, we also used a compound whose structure and stoichiometry are well determined[12] as a secondary standard, single crystals of $GdCr_3S_6$. Comparison of columns 1 and 2 for $GdCr_3S_6$ (Table 1) shows that microprobe analysis and theoretical composition fit together very well; the small discrepancy of analysis 1 relatively to analysis 2 has been used to adjust the second set of analyses for "$GdCrS_3$" (B of Table 1).

Table 1 gives the results of the microprobe measurements on a crystal of the "$GdCrS_3$" misfit compound. On the basis of S = 3.27 atoms, according to the crystallographic data, this analysis gives the structural formula $Gd_{1.162(11)}Cr_{0.995(8)}S_{3.27}$. If a perfect segregation of the Gd and Cr between the two types of layers is assumed, the results imply a structural formula of $(Gd_{1.16}\square_{0.11}S_{1.27})CrS_2$. While some metal antisite defects may occur, we expect the density of these to be low, since the Cr and Gd have very different sizes. The ratio of their ionic radii in six-fold coordination is $Gd^{3+}/Cr^{3+} = 1.54$. Within experimental error, this composition leads to an exact balance of the trivalent cationic charges on Gd and Cr by the divalent anionic charge on the sulfur. Consequently, no excess electrons exist and semiconducting behavior is expected, since the d^3 electron configuration on Cr^{3+} is localized to form a magnetic moment (i.e. a Mott insulator is obtained).

Similar results are obtained for "$LaCrS_3$" and "$YCrS_3$" (see Table 1). For both of them it is clear that a large number of vacancies must occur on the rare earth site. However, since we have not used a ternary sulfide as a secondary standard for these two compounds, the possible error in the metal stoichiometry is about twice as large as that for the "$GdCrS_3$" sample. For example, the obtained composition for "$YCrS_3$" is $Y_{1.20}Cr_{1.01}S_{3.28}$. Again, within the larger experimental error, the cationic and anionic charges balance and no excess electrons remain.

For "$LaCrS_3$", the vacancy ratio is identical to that of the formula proposed by Kato *et al.*,[2] but without any Cr atom in the [MS] layer. This model does not have the contradictions pointed out by Makovicky *et al.*[13] and Otero-Diaz *et al.*,[14] and contradicts the hypothetic noninteger average valency +2.91 for cations proposed by Otero-Diaz.

Revised Structural Refinement

In light of the above analyses, we redid the refinement of the misfit structure of "$GdCrS_3$". In this new refinement, we let the occupancy of the rare earth site vary and also allow for the possibility of antisite defects.

There are now two methods which can be used to determine the structure of the misfit compounds. In the first method, the two sublattice model, the reflections are split into three groups: those due to the [CrS_2] sublattice alone, those due to the [GdS] sublattice alone, and the common reflections (the 0*kl* set, which is independent of the two incommensurate *a* parameters). In general, a fourth set of reflections may be present. These are superlattice reflections due to the modulation of one sublattice by the other. Since these reflections are usually weak and since other defects, such as stacking faults, smear them out, highly perfect crystals are necessary to see these reflections. In the case of "$GdCrS_3$", the crystal perfection is not high enough to see these superlattice reflections.

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Table 1. Electron Microprobe Analysis of (Ln–Cr) Sulfides

	$GdCr_3S_6$ (n = 11)[c]		"$GdCrS_3$" (A)[a] (n = 19)		"$GdCrS_3$" (B)[b] (n = 8)		"$YCrS_3$" (n = 23)		"$LaCrS_3$" (n = 11)
phase	% (1)[d]	% (2)[e]	% (1)	(3)[f]	% (1)	(3)	% (1)	(3)	% (1)
Ln	31.14(27)	31.10	53.94(21)	1.164(10)	53.74(36)	1.162(11)	40.02(29)	1.199(12)	50.12(25)
Cr	30.74(18)	30.85	15.75(12)	1.027(9)	15.22(9)	0.995(8)	19.72(12)	1.010(10)	16.78(13)
S	37.57(22)	38.05	30.91(22)	3.27	30.85(15)	3.27	39.50(25)	3.28	31.36(26)[g]
Σ	99.45	100	100.60		99.81		99.24		98.26
Ln/Cr			1.133(13)		1.168(15)		1.187(16)		1.118(14)

[a] (A): first set for "$GdCrS_3$". [b] (B): second set for "$GdCrS_3$" with $GdCr_3S_6$ as internal standard. [c] n: number of spot analyses. [d] (1): weight% with standard deviation in parentheses. [e] (2): theoretical weight % for $GdCr_3S_6$. [f] (3): structural formula (S fixed on the basis of crystallographic data). [g] Low value for S content.

Table 2. Crystal Data and Details of the Data Collection Conditions[a]

General Data	
fw	339.26 g/mol
ρ_{obsd}	5.3(3) g·cm^{-3}
ρ_{calcd}	5.23 g·cm^{-3}
μ	221 cm^{-1}
T	20 °C
[GdS] Part	
sym	orthorhombic
a_1	5.454(1), 5.8098(6), 21.461(4) Å
radiation (λ)	Mo Kα (0.7107 Å)
θ range	1.5–35°
ω scan	$\Delta\omega = 1.30 + 0.35 \tan \theta$
no. of reflcns ($I \geq 3\sigma(I)$, $h \neq 0$; $(\sin \theta)/\lambda \leq 0.75$)	m = 327
no. of variables	n = 13
R_F, wR_{F^2}, S	0.054, 0.062, 1.65
highest resid peak in final Fourier map	±2.6 e·Å^{-3}
Common Part	
no. of reflcns ($I \geq 3\sigma(I)$, $(0kl)$)	m = 79
no. of variables	n = 10
R_F, wR_{F^2}, S	0.059, 0.056, 1.72
highest resid peak in final *Fourier* map	±0.502 e·Å^{-3}

[a] $R_F = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_F = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$, and $S = (\sum w(|F_o| - |F_c|)^2/(m - n))^{1/2}$.

Table 3. Positional and Thermal Parameters for the [GdS] Part of "$GdCrS_3$"

atom	site	x	y	z	sof (%)	B_{eq} (Å^2)
				Condition *a*		
Gd	8(f)	0	0.1631(2)	0.17047(6)	100	1.94(2)
S1	8(f)	$^1/_2$	0.161(1)	0.1998(2)	100	1.25(8)
				Condition *b*		
Gd	8(f)	0	0.1631(2)	0.17048(6)	95.7(3)	1.94(2)
S1	8(f)	$^1/_2$	0.161(1)	0.1998(2)	100	1.40(8)

[a] sof (sof = site occupancy factor) not refined; R = 0.0542. [b] sof for Gd refined; R = 0.0537.

Table 4. Positional and Thermal Parameters for the Common Part of "$GdCrS_3$"

atom	site	x	y	z	sof (%)	B_{iso} (Å^2)
				Condition *a*		
Gd	8(f)		−0.08790(-)	0.17039(-)	63.6	1.08(4)
S1	8(f)		−0.0895(5)	0.1997(1)	63.6	0.5(2)
Cr	4(a)		0	0	100	0.08(9)
S2	8(f)		0.168(2)	0.0633(2)	100	0.27(9)
				Condition *b*		
Gd	8(f)		−0.08778(-)	0.17040(-)	58.3(4)	0.97(4)
S1	8(f)		−0.0894(5)	0.19974(9)	58.3(-)	0.5(2)
Cr	4(a)		0	0	100	0.37(9)
S2	8(f)		0.167(1)	0.0633(2)	100	0.53(9)
				Condition *c*		
Gd	8(f)		−0.08779(-)	0.17034(-)	58.0(4)	0.94(4)
S1	8(f)		−0.0895(5)	0.1997(1)	63.6	0.8(2)
Cr	4(a)		0	0	100	0.37(9)
S2	8(f)		0.168(-)	0.0633(-)	100	0.54(9)

[a] sof fixed; R = 0.0664. [b] sof for Gd and S kept equal and refined; R = 0.0593. [c] sof for Gd free; R = 0.0582.

The second refinement approach is the superspace method.[15] In this case all the data are used at once and the superlattice reflections determine the amplitude and relative phases of the modulation of one lattice by the other. These modulations can be quite large, on the order of 0.1 Å. However, as mentioned already, the crystal quality is not sufficient to obtain these modulations, so we use here the "two sublattice method" to look for structural evidence of the Gd vacancies.

For this, a single crystal was mounted on an Enraf-Nonius CAD-4 diffractometer with Mo Kα radiation and a graphite monochromator. Crystal data and details of data collection are given in Table 2. The structure, using the composite approach, was solved by Patterson and Fourier methods and refined by full-matrix least-squares methods. All calculations were performed with MOLEN chain programs.[16]

The results obtained from the [CrS_2] sublattice are identical to those obtained previously.[3] The important information about the Gd vacancies is expected to be observable in the analysis of the [GdS] part and the common part. We discuss these next.

The refinement of the [GdS] sublattice was carried out in the *Cmca* space group. When the occupation of the Gd and S sites is fixed at 100%, the refinement of the [GdS] sublattice reflections results in a reliability factor of R = 0.0542 for 327 reflections and 13 variables (see Table IIIa). Surprisingly, when the occupation of the Gd site alone is allowed to vary, the R factor is not improved within experimental error (R = 0.0537 for the same reflections now with one more parameter, the Gd site occupancy, which is determined to be 95.7%) (Table 3b). From these reflections alone nothing can be said about the vacancy concentration. This lack of direct evidence for vacancies in the GdS sublattice may be due to two factors: the modulation of the GdS sublattice and anisotropic vibration of the Gd, especially near the defects.

Interestingly, the evidence for vacancies is clearly visible in the common reflections ($0kl$). If the ratio of [GdS] to [CrS_2] is fixed by the ratio of the $\vec{a}$ axis parameters and 100% occupation of the Gd and S sites is assumed, a reliability factor of 0.0664 is obtained (79 reflections, 7 variables). The relative diffracting power of the two sublattices is 0.636:1.00 GdS:CrS_2 (see Table 4a). If the occupation of the [GdS] sublattice is allowed to decrease, but the ratio of Gd to S is fixed at 1:1, the R factor improves to 0.0593 and the diffraction power of the [GdS] sublattice drops to 58.3% relative to that of [CrS_2] (Table 4b), giving the chemical formula of $(GdS)_{1.17}CrS_2$, as reported previously.[3] Finally, if the vacancies are confined to the Gd sites alone, the R factor improves slightly, to 0.0582 for the same number of variables (Table 4c), and the chemical formula obtained is $(Gd_{1.16}S_{1.27})CrS_2$, a formulation that is identical to that obtained from the microprobe.

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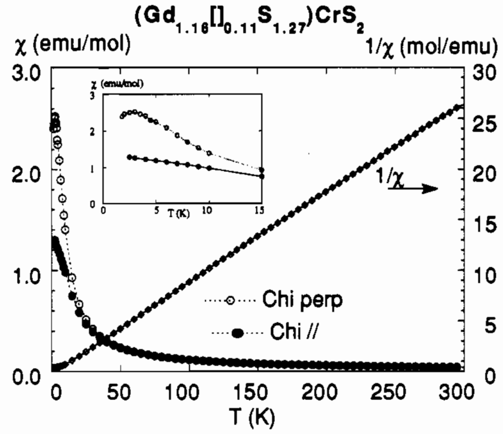

Figure 2. χ and $1/\chi$ versus T plots for "$GdCrS_3$". The measurements were made on several single crystals. The magnetic field (H = 100 Oe) is applied parallel ($\chi_{\parallel}$) or perpendicular (χ_{perp}) to the c axis.

Both vacancy models offer a clear improvement in the refinement, with a slight preference for only Gd vacancies. However only the latter model, Gd vacancies alone, is consistent with the analytical data and is therefore the preferred model. It is clear that the combined data show that the [GdS] layer is highly defective, with a large number of Gd vacancies.

Density Measurements

In order to prove the correctness of the presence of Gd vacancies we performed density measurements (Micrometrics ACCUPYC 1320 pycnometer) on several single crystals (m = 0.0379 g). Because of the small amount of crystals, the accurancy of the density value is poor: d = 5.3(3) g·cm^{-3}. This result, however, is not inconsistent with the hypothesis of Gd vacancies: $d_{expected}$ = 5.28 g·cm^{-3} which is to be compared with the density value assuming no vacancy (d = 5.49 g·cm^{-3}).

Physical Properties

The magnetic susceptibility of "$GdCrS_3$" has been determined from 4 to 300 K on a sample consisting of a few milligrams of microcrystals using a squid magnetometer. Figure 2 shows χ and $1/\chi$ as a function of temperature. The compound is clearly paramagnetic as expected for local moments on both the Cr and Gd. The data fit the Curie–Weiss law, $\chi = C/(T + \theta) + \chi_o$, from 50 to 300 K. We used a calculated value for χ_o (-1.5×10^{-4} emu/mol for the core diamagnetism) to obtain $\theta = -1.5$ K. Since the Gd moment is large, χ_o is a negligible fraction of the susceptibility at all temperatures. The effective magnetic moment calculated from the Weiss constant C is μ_{eff} = 9.46 μ_B (by comparison to other standards and some correction for sample shape, we estimate the error in moment to be ±0.2). The theoretical squared effective moment (per formula unit of $Gd_{1.16}Cr_{1.00}S_{3.27}$) is proportional to sum of $Ng^2S(S + 1)$ for both cations, where N is the number of moles of each cation. Note that for both trivalent cations we expect $g = 2$ and spin only moments (L = 0 for Gd^{3+}). The effective moment calculated from this sum, μ_{eff}, is 9.39 μ_B, a value that within experimental error is equal to the measured value. Even though the results are very close, this magnetic susceptibility measurement cannot be used to determine the percentage of Gd vacancies in this compound. Because the sample is very anisotropic (stacking of layered crystals), the experimental data have to be corrected by an empirical factor. This results in a decrease of the precision of the susceptibility value (≈5%). An error calculation shows that under these conditions the molar fraction of Gd cannot be determined very precisely. Therefore, it can be said that the results are not in contrast to the existence of vacancies found by microprobe analysis. The chemical analysis technique is the most reliable and the most precise in this context.

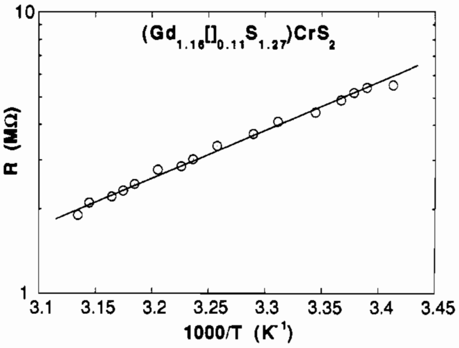

Figure 3. Electrical resistance versus $10^3/T$ measured on a single crystal of "$GdCrS_3$".

When a single-crystal sample is oriented in the magnetic field with H parallel and perpendicular to $\vec{c}$, an anisotropy becomes evident below 30 K and some evidence of magnetic order is seen near 3 K (Figure 2). Although a maximum is seen in the susceptibility near 3 K (see inset to Figure 2), no sharp change in behavior is noted, so that the nature of the magnetic state is not as clear as for the metallic compound "$GdNbS_3$", where a "classical" transition to an antiferromagnetic state is observed.[17,18] Further, the susceptibility of "$GdCrS_3$" is the same if the sample is cooled in zero field or in the measuring field, in contrast to the large difference for the different cooling conditions in the susceptibility of "$LnCrS_3$" when Ln = La or Nd.[19]

The plot of the electrical resistance versus $1000/T$ is shown in Figure 3. "$GdCrS_3$" presents a very large resistivity at room temperature (≈10^4 Ω cm) and a semiconducting behavior. Low-temperature measurements were not performed because the sample shows a high electrical resistivity. Nevertheless, this result agrees very well with the assumption of the absence of free electrons made above.

Discussion and Conclusion

The stoichiometry and structure of the misfit compounds determine their electrical and magnetic properties. Unless novel phenomena are at play, the properties in turn should be "predictable" from the composition and structure of the materials as well as from the behavior of closely related compounds.

As a first approximation, we consider the composition $(MX)_xTX_2$ (with X = S, Se) and suppose that the properties can be predicted by considering separated layers. The $[TX_2]$ layer can be expected to behave in a manner similar to the parent compound, with the Fermi level suitably raised higher in the d band to account for any charge transfer from the [MX] layer. Similarly, the [MX] layer can be expected to behave as the parent MX compound again taking into account any charge transfer. In general then, $[TX_2]$ layers where T = Ti, Zr, Hf, or V (in all these cases T is octahedrally coordinated) should be metallic independent of the charge transfer, as long as it is not zero. When T = Nb or Ta the metal is in trigonal prismatic coordination and again metallic behavior of those layers is expected, unless the charge transfer is exactly one electron per $[TX_2]$ unit. The case of Cr is a little different, since simple band calculations would predict metallic behavior for $LiCrS_2$,[20] but magnetic semiconductors (Mott insulators) are obtained instead. The [MX] layers should also be metallic as are the parent NaCl structure materials (if they exist), unless the charge transfer is exactly one electron per rare earth. In such a simple picture all of the misfit compounds should be metallic.

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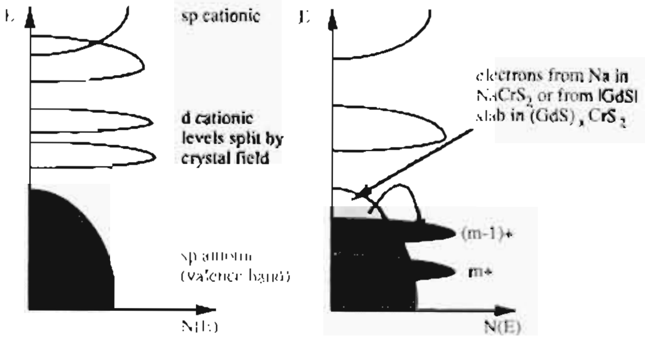
This picture must be modified in several ways in order to achieve a better expectation of the true properties. First, we now know that the [MX] layer is likely to be nonstoichiometric. This will change the electron count and the position of the Fermi level. Second, the random potential produced by any vacancies in the rare earth layer may produce Anderson localization. Finally, changes in the interatomic distances can lead to modified behavior. These changes are of two types: the average change due to the misfit strains and the periodic modulation of those distances resulting from the beating of the two different periodicities of the [MX] and [TX$_2$] layers, "strain waves".

In the present instance concerning the "GdCrS$_3$" misfit compound, we have already pointed out that the Gd vacancies in the [GdS] layer are consistent with the observed semiconducting behavior. Without Gd vacancies, there are 0.27 excess electrons if Gd^{3+} and Cr^{3+} are assumed. We expect that the d^3 electron configuration of Cr^{3+} will result in Mott localization as in LiCrS$_2$ and a spin of $^3/_2$ per Cr. But the excess electrons should lead to metallic behavior. This former puzzle is now solved by the Gd vacancies, which account within experimental error for those electrons and lead us to expect semiconducting behavior as observed. This suggests that all the Cr misfit compounds have Cr^{3+} and just the right number of rare earth vacancies so that with trivalent rare earth cations there are no excess electrons. This overall picture is consistent with the magnetic properties of "GdCrS$_3$" as well, although the large Gd^{3+} moment makes an accurate determination of the Cr^{3+} moment difficult. However, in the semiconducting compound "LaCrS$_3$" exactly the expected moment for Cr^{3+} is observed,[18] as predicted from both the vacancy model and Mott localization. If indeed the vacancy concentration is not exactly the number needed to produce a semiconductor, so that a small number (smaller than 0.27 in the case of "GdCrS$_3$") of excess electrons remain, the random potential of the vacancies could localize the remaining few. But it is clear that the rare earth vacancies are the main electron-balancing mechanism.

The low-temperature magnetic properties, where magnetic exchange effects dominate, are more complicated. In the case of the "GdCrS$_3$" misfit compound, both the Gd and Cr have magnetic moments. It is also known that the exchange energy in intercalated CrS$_2$ compounds is a sensitive function of the Cr–Cr distance. Since both the vacancies and the strain wave modulate all the cation distances (in the case of the Cr–Cr distances by more than 0.1 Å), the magnetic response is expected to be complex, with possible spin glass-like behavior. Such behavior is observed in the "LaCrS$_3$" below about 70 K but is not apparent in "GdCrS$_3$" above 2 K.

The V compounds remain puzzling. It could be that the modulation of the V–V distances induces Mott localization, which should produce a magnetic moment of spin 1 and easily be detectable in magnetic properties. Anderson localization could result from the expected vacancies in the [MX] layer. It seems unlikely that the strain wave modulation of 0.1 Å alone could result in semiconducting behavior of an otherwise metallic compound. This is so since the modulation is in only one dimension and would produce band gaps only in directions close to the modulation direction (assuming that these gaps are not several eV wide but are small which would be consistent with the small modulation and the metallic appearance of the samples). In any case, it is essential that the exact stoichiometry and defect distribution of the compounds are determined and that the magnetic properties are measured, before a complete understanding of those phases can result.



(a) (b)

Figure 4. Schematic representation of the band structure of transition metal dichalcogenides. (a) The valence band is essentially sp anionic in character. The corresponding sp cationic levels have been pushed up. The d cationic levels which are split by a crystal field are positioned between those two bands. (b) On the right side of a period the d levels have a progressively lower energy than on the left side thereby sometimes overlapping the sp valence band. Empty d levels will be filled at the expense of the sp band at the top of which holes will appear. This process is essentially a reduction of the cation (Cr^{3+} and even Fe^{2+} are stable in the presence of sulfur but not Ti^{4+} for titanium). In addition, because the top of such a band has antibonding character, the anions are now positioned closer to each other, leading at the limit to the formation of anionic pairs like in pyrites or marcasites. Ti^{4+} is stable in the presence of sulfur whereas Cr^{4+} is not. However, because of the electronic transfer from the [GdS] slab to the [CrS$_2$] slab, the sp band remains full thereby preventing the formation of anionic pairs. In this case the electronic transfer is necessary to stabilize the [CrS$_2$] layers.

So far we have not been able to prepare MCrS$_3$ misfit compounds with M = Pb or Sn, nor have any been reported. It is instructive to note that, while intercalation compounds such as LiCrS$_2$ or AgCrS$_2$ are well known,[21] the parent layered phase CrS$_2$ is unknown. In binary or ternary chromium sulfides the maximum oxidation state achievable is +3. Since the Cr-d^3 electronic state lies below the top of the sulfur valence band, attempts to oxidize Cr lead to oxidation of the sulfur and holes at the top of the valence band (Figure 4). The existence of these holes in sulfides usually leads to the formation of sulfur–sulfur bonds in the structure or to the loss of elemental sulfur, depending upon reaction conditions. Consequently, it appears that the transfer of one electron from the [MS] layer to the [TS$_2$] layer is necessary for the stability of the Cr misfit compounds. Since it has been found that the charge transfer to [TiS$_2$] or [NbS$_2$] layers is small when M = Pb or Sn,[1] it is unlikely that these elements could stablize the Cr misfit compounds. Further, in contrast to CrS$_2$, the parent [TS$_2$] layers for T = Ti, Nb, or Ta are stable on their own and electron transfer is not necessary for their stability. In this case, even a weak interaction and small electron transfer can still lead to intercalation compounds or misfit compounds. On the other hand when M = Ln, each cation has one extra electron that apparently is at high enough chemical potential to be donated to the [TS$_2$] layer, leading to the existence of the Cr misfit compounds.

Even though the electronic transfer to the layers is known to be small when M = Pb or Sn and T = Ti, Nb, or Ta, some questions remain concerning the electronic structure of these compounds. If the [MX] layer is stoichiometric, transfer of electrons to the [TX$_2$] layer should leave holes in the [MX] layer that would produce metallic conduction in the absence of Anderson localization. Such holes should result in a rather low anisotropy in electrical conductivity and be apparent in measurements of the thermopower or Hall effect. On the other hand, given that we now know that the [MX] layer can support a considerable density of defects, it is possible that the charge transfer to the layers is compensated for by sulfur vacancies. In that case such compounds would have the following structural formulation: $(MS_{1-y}\square_y)_xTS_2$, with $2 \times x \times y$ electrons donated to the [TS$_2$] layer. Further, the [MS] layer would then be semiconducting leading to a large electrical anisotropy as has been reported in a few cases and to a one carrier model for conduction in the [TS$_2$] layers. Experiments are underway in order to test this hypothesis.

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Experimentally, for the materials examined so far, it is found that the compounds of Ti, Nb, and Ta are metallic, while those of Cr are semiconducting. The situation for V is confusing, since different groups report different properties and in the case of $(SmS)_xVS_2$ two different results are reported by the same group on different crystals of the "same" material. We have reported here that the [MS] layer can support a high density of vacancies which have a controlling effect on both the chemistry and the physical properties. Consequently, it appears that the misfit compounds need further study, especially in light of the findings reported in this paper.

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