Metal−Metal Bonding and Correlated Metallic Behavior in the New Deficient Spinel $Ga_{0.87}Ti_4S_8$

C. Vaju, J. Martial, E. Janod, B. Corraze, V. Fernandez, and L. Cario*

Institut des Matériaux Jean Rouxel (IMN), Université de Nantes, CNRS, 2 rue de la Houssinière, BP3229, 44322 Nantes, France

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We have synthesized and characterized the first Ti member of the AM_4X_8 (A = Ga, Ge; M = V, Nb, Ta, Mo, X = S, Se) family of compounds that exhibit a deficient spinel structure with tetrahedral transition metal clusters. Single-crystal X-ray structure determination of $Ga_{0.87}Ti_4S_8$ (space group $F-43m$, a = 9.9083(11) Å) revealed the presence of Ga vacancies and a partial declustering of the transition metal atoms compared to other members of the family. This declustering is likely associated to the decrease of the electronic filling of the clusters from 7 to 11 electrons in known AM_4X_8 compounds to ~3 electrons in $Ga_{0.87}Ti_4S_8$. XPS measurements show that the valence band of $Ga_{0.87}Ti_4S_8$ is more dispersed than that of the Mott insulator GaV_4S_8, which suggests a strengthening of the transfer integrals induced by the slackening of the transition metal clusters. A Fermi step consistent with a metallic character is observed in $Ga_{0.87}Ti_4S_8$ while a gap appears (0.2 eV) below the Fermi level in the Mott insulator GaV_4S_8. The resistivity measured on crystals of $Ga_{0.87}Ti_4S_8$ showed a metallic behavior with a small residual resistivity ratio. $Ga_{0.87}Ti_4S_8$ exhibits large electronic specific heat ($\gamma = 58$ mJ K^{-2} mol^{-1}) and Pauli susceptibility. All these measurements as well as the Wilson and Kadowaki-Woods ratios demonstrate that $Ga_{0.87}Ti_4S_8$ exhibits a correlated metal type behavior and is no longer a paramagnetic Mott insulator like other members of the family.

1. Introduction

Oxide spinels have been extensively studied in the last decades as they present very interesting properties, like good electrochemical performance,[1] superconductivity,[2] or heavy fermion behavior.[3] The less notorious chalcogenide spinels present also an attractive variety of structural, electrical and magnetic properties. For example, $CuIr_2S_4$ exhibit a metal–insulator transition,[4] $CuRh_2S_4$ is the first compound to show a pressure-induced superconductor−insulator transition,[5] and the Cr-based chalcogenide spinels exhibit magnetoresistance.[6] Recently, pressure induced insulator–metal transition and superconductivity was also reported in the spinels GaM_4Se_8 (M = Ta, Nb).[7,8] These ternary chalcogenides belong to an interesting class of transition metal systems of formula AM_4X_8 (with A = Ga, Ge; M = V, Nb, Ta, Mo; X = S, Se) which exhibit a cubic structure of the $GaMo_4S_8$-type that is often described as a cation-deficient spinel.[9] In these compounds the tetrahedral sites are only half-occupied by the A atoms, which leads to a formula AM_4X_8 instead of AM_2X_4 and lowers the symmetry from $Fd\bar{3}m$ to $F\bar{4}3m$. But the most interesting structural features compared to the regular spinels are the shift of the metal atom M off the center of the octahedral site, and the subsequent formation of tetrahedral M_4 clusters containing 7−11 electrons. Within these clusters the M-M distances are compatible with the formation of metallic bonds, while the large intercluster distances prevent metal−metal bonding. This peculiar topology leads to the formation of molecularlike electronic states within the clusters. So far, the AM_4X_8 compounds were all found to be insulators at ambient pressure,[10,11] and are considered as Mott insulators.[7,12,13] A so-called Mott insulator is a compound where the electron are localized because the on site Coulombic repulsion energy (called the Hubbard energy U) is too high compared with the kinetic energy (i.e., the transfert integral t).[14] Interestingly the AM_4X_8 represents a special type of Mott insulators in which the electronic Coulombic repulsion giving rise to the Mott-Hubbard gap takes place not on a single atom but on a small cluster.[7,12,13] Usually Mott insulator compounds can be brought to the metal–insulator transition either by application of an external pressure which increases the kinetic energy between neigh-

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* Corresponding author. E-mail: Laurent.cario@cnrs-imn.fr.

(1) Tarascon, J. M.; Wang, E.; Shokoohi, F. K.; McKinnon, W. R.; Colson, S. *J. Electrochem. soc.* **1991**, *138*, 2859–2864.
(2) Johnston, D. C. *J. Low Temp. Phys.* **1976**, *25*, 145.
(3) Kondo, S. *Phys. Rev. Lett.* **2007**, *78*, 3729.
(4) Furubayashi, T.; Matsumoto, T.; Hagino, T.; Nagata, S. *J. Phys. Soc. Jpn.* **1994**, *63*, 3333–3339.
(5) Hagino, T.; Seki, Y.; Wada, N.; Tsuji, S.; Shirane, T.; Kumagai, K. I.; Nagata, S. *Phys. Rev. B* **1995**, *51*, 12673–12684.
(6) Ramirez, A. P.; Cava, R. J.; Krajewski, J. *Nature* **1997**, *386*, 156–159.
(7) Abd-Elmeguid, M. M.; Ni, B.; Khomskii, D. I.; Pocha, R.; Johrendt, D.; Wang, X.; Syassen, K. *Phys. Rev. Lett.* **2004**, 93.
(8) Pocha, R.; Johrendt, D.; Ni, B. F.; Abd-Elmeguid, M. M. *J. Am. Chem. Soc.* **2005**, *127*, 8732–8740.
(9) Ben Yaich, H.; Jegaden, J. C.; Potel, M.; Sergent, M.; Rastogi, A. K.; Tournier, R. *J. Less-Common Met.* **1984**, *102*, 9.
(10) Pocha, R.; Johrendt, D.; Pöttgen, R. *Chem. Mater.* **2000**, *12*, 2882–2887.
(11) Johrendt, D. *Z. Anorg. Allg. Chem.* **1998**, *624*, 952–958.
(12) Muller, H.; Kockelmann, W.; Johrendt, D. *Chem. Mater.* **2006**, *18*, 2174–2180.
(13) Jakob, S.; Muller, H.; Johrendt, D.; Altmannshofer, S.; Scherer, W.; Rayaprol, S.; Pottgen, R. *J. Mater. Chem.* **2007**, *17*, 3833–3838.
(14) Imada, M.; Fujimori, A.; Tokura, Y. *Rev. Mod. Phys.* **1998**, *70*, 1039.

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boring sites or by chemical doping.[14] So far the literature lacks of studies on chemical doping of the AM_4X_8 compounds, but as said above a pressure induced metal–insulator transition was already observed in these compounds.[7,8] This transition was related to the decrease of the shift of the transition metal atom M off the center of the chalcogenide octahedral site. Another way to achieve this, was recently reported by Bichler and Johrendt,[15] who were able to tune the metal-metal bonding within the M_4 clusters up to complete declustering via electron count (7−12) in the $Ga_xV_{4-x}Cr_yS_8$ series. The release of the clustering via electronic filling could in principle also restore a metallic character. However, chromium remains as Cr^{3+} ions in these compounds like in other Cr-based chalcogenides[16] and a metallic character was not observed within this series. On the other hand, using other transition elements with more diffuse 3d orbitals like Ti could open the door to metallic or superconducting AM_4X_8 compounds.

In this paper we explore the structural and electronic properties of the first Ti member of this family containing only ∼3 electrons per cluster. Our single crystal X-ray structure determination confirmed that $Ga_{0.87}Ti_4S_8$ crystallizes in a deficient spinel type structure with a partial declustering of the metal atoms compared to other member of the AM_4X_8 family. X-Ray Photoemission Spectroscopy, magnetic susceptibility and specific heat measured on $Ga_{0.87}Ti_4S_8$ demonstrate that this compound is no longer a Mott insulator but exhibits a correlated metal character. A comparison with data measured on crystals of the Mott insulator GaV_4S_8 is presented.

2. Experimental Section

Preparation. A pure precursor phase Ga_2S_3 was first obtained by heating Ga_2O_3 at 1073 K for 8 h under H_2S flow. The samples were then prepared by heating of stoichiometric mixtures of Ga_2S_3, titanium and sulfur (purities >99.99%) to 1223 K at 300 K/h for 24 h in sealed glass tubes under small residual pressure ($<1 \times 10^{-5}$ bar). This synthesis yielded dark gray powders stable when exposed to air or humidity. Single crystals were obtained when a small amount of iodine (∼4 mg/cm^3) was added to the stoichiometric mixtures to favor vapor transport crystallization. In this latter case, the mixtures were heated to 1263 K at 50 K/h for 8 days in quartz ampoules of about 10 cm length.

Chemical Analysis. Semiquantitative chemical analyses were performed with the use of a scanning electron microscope JEOL 5800 equipped with a microanalyzer on different single crystals. We observed average atomic percentages 6.15(19), 31.45(11), 62.40(14) for Ga, Ti, and S, respectively. This leads to a formula $Ga_{0.78(2)}Ti_{4.00(1)}S_{7.94(2)}$ suggesting a slight deficiency of Ga compared to the ideal composition $Ga_1Ti_4S_8$.

Single-Crystal X-ray Data Collection and Structure Refinement. Single crystal diffraction experiments were performed using a four circles FR 590 Nonius CAD-4F Kappa-CCD diffractometer at room temperature, using Mo Kα radiation (0.071069 nm wavelength). Numerous crystals were tested for quality (intensity and shape of the spots) and the best crystal was selected for subsequent data collections. A set of 190 frames was collected in ω scan mode, with a rotation of 2° and an exposure time of 40 s per frame; the crystal-to-detector distance was 25 mm. The reflection set was consistent with the cubic space group $F\bar{4}3m$.

Table 1. Crystallographic Data, Experimental Details and Refinement Results for the Structure of $Ga_{0.87}Ti_4S_8$

crystallographic data	
chemical formula	$Ga_{0.87}Ti_4S_8$
mol wt (g mol^{-1})	508.7
symmetry	cubic
space group	$F\bar{4}3m$
a (Å)	9.9083(11)
V (Å^3)	972.74(19)
Z	4
density (g/cm^3)	3.473
cryst dimensions (μm^3)	$160 \times 120 \times 100$
data collection and reduction	
T (K)	293
eavelength (Å)	0.71069
$F(000)$	972
θ (deg) range	{6.83–34.62}
h, k, l ranges	$-14 < h < 12$; $-15 < k < 15$; $-14 < l < 12$
collected reflns	4090
independent reflns	251
obsd reflns ($I > 3\sigma(I)$)	244
abs corr	Gaussian integration method
abs coeff (mm^{-1})	7.171
T_{min}/T_{max}	0.383/0.557
R_{int}	0.0955
refinement results	
refinement method	least square on F^2
$F(000)$	736
data/restraints/params	251/ 0/ 13
reliability factor	$R_{obsd} = 0.0235$; $R_{all} = 0.0246$
weighted reliability factor	$R_{wobsd} = 0.0503$; $R_{wall} = 0.0505$
electronic residues (e$^-$/Å^3)	0.88/−1.42

All data treatments, refinement, and Fourier synthesis were carried out with the JANA2000 chain program.[17] Data were corrected for Lorentz and polarization effects and secondary extinctions correction was applied. The absorption correction was performed using an analytical method taking into account the crystal dimensions by face indexation. The initial set of 4090 reflections was averaged according to the $m3m$ point group leading to 251 independent reflections (all data) with $R_{int} = 0.0954$.

The structure was refined by considering the atomic coordinates found by Pocha et al. [8] for GaV_4S_8. Using these positions, the full-matrix least-squares refinement of the structure converged straight to $R_{obs} = 2.95\%$ for 245 observed reflections ($I > 3\sigma(I)$) and 12 variables. At this stage, we took into account the results of the chemical analysis suggesting a Ga nonstoichiometry and we refined the site occupancy factor on the Ga site. This led to a further improvement of the refinement ($R_{obs} = 2.38\%$ for 13 variables) and a much better agreement between analyzed $Ga_{0.78(2)}Ti_{4.00(1)}S_{7.94(2)}$ and refined $Ga_{0.87(1)}Ti_4S_8$ chemical formulas. On the other hand, our trial to refine a partial Ga-occupation of the second tetrahedral site led to a site occupancy that did not depart from 0 within the standard deviation.

All details about the data collections and structure refinement are gathered in Table 1. The refined atomic position and displacement parameters are given in Table 2.

X-ray Powder Diffraction. X-Ray powder diffraction data collections were performed at room temperature in the 10–120° 2θ range on a Bruker D8 Advance Diffractometer using Cu Kα1 radiation. The powder pattern of the $Ga_{0.87}Ti_4S_8$ sample did not show any evidence of known major phases and revealed the

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(15) Bichler, D.; Johrendt, D. *Chem. Mater.* **2007**, *19*, 4316–4321.

(16) Cario, L.; Johrendt, D.; Lafond, A.; Felser, C.; Meerschaut, A.; Rouxel, J. *Phys. Rev. B* **1997**, *55*, 9409–9414.

(17) Petricek, V.; Dusek, M.; Palatinus, L. *JANA2000*,03/02/2005; Institute of Physics: Praha, Czech Republic, 2005.

Table 2. Fractional Atomic Coordinates, and Main Interatomic Distances Obtained from the Refinement of $Ga_{0.87}Ti_4Se_8$.

Atomic Positions

atom	Wyckoff	*x*/*a*	*y*/*b*	*z*/*c*		U_{eq}
Ga	4a	0	0	0		0.00783(19)
Ti	16e	*x*	*x*	*x*	$x = 0.61384(6)$	0.01161(13)
S1	16e	*x*	*x*	*x*	$x = 0.62628(6)$	0.00969(14)
S2	16e	*x*	*x*	*x*	$x = 0.13185(6)$	0.00750(15)

Main Interatomic Distances

atom 1	atom 2	distance (Å)
Ga	S2 ×4	2.2628(6)
Ti	Ti ×3	3.1904(8)
Ti	Ti ×3	3.8158(8)
Ti	S1 ×3	2.3856(8)
Ti	S2 ×3	2.5323(8)

presence of Ga_2S_3 as a side product. The Powder cell program was used to simulate the powder pattern using as structural model the structure refined from the single crystal study.[18] The comparison shows that the powder and the single crystal have similar X-ray diffraction patterns and therefore that the synthesis of $Ga_{0.87}Ti_4S_8$ yielded a powder of good purity (see figure 1).

X-ray Photoemission Spectroscopy. We performed XPS measurement using a Kratos Axis Ultra spectrometer using the monochromatic Al Kα X-ray source (1486.6 eV) at 150 W. These experiments were carried out on single crystals of $Ga_{0.87}Ti_4S_8$ and of GaV_4S_8 cleaved ex situ just prior their introduction in the vacuum chamber. To maximize the signal during the measurements, the samples were attached with a carbon paste to 17 μm gold wires and subsequently placed above a hole made in the sample holder. The surface analyzed during these experiments was $110 \times 110\ \mu m^2$ (mode 110μm). As the binding energy measured with the dispersive monochromatic Al X-ray source slightly depends on the sample position, we also measured for calibration the same sample using the standard Al source. Data obtained with the standard source are indeed sample position-independent and allow an accurate calibration of the binding energies. The instrumental resolution during this work (mode 110 μm) was determined using the silver Fermi edge. The 12−88% width of the Fermi edge is in these conditions 0.57 eV.

Electrical Measurements. Electrical resistivity of $Ga_{0.87}Ti_4S_8$ was measured using a four-point probe method on single crystals. The crystals dimension was around 200–300 μm. We used 10 μm gold wires electrodes that were fixed on the sample thanks to a carbon paste annealed at 473K for 2 h under vacuum. The measurements were performed between 300 and 1.5 K at bias smaller than 0.01V.

Specific Heat. Calorimetric measurements were performed on a homemade specific heat setup using the semiadiabatic method in the temperature range 4–20 K. Data recorded on a sintered pellet pasted with General Electrics varnish were corrected for the sample holder contribution.

Magnetic Measurements. We performed magnetic studies using a Quantum Design MPMS SQUID magnetometer in the 300K-1.5K temperature range. Zero field-cooled (ZFC) and field-cooled (FC) susceptibility were measured on a powder samples of $Ga_{0.87}Ti_4S_8$ ($m = 135.15$ mg) and of GaV_4S_8 ($m = 142.47$ mg) under an applied field of 1000 Gauss. Data were corrected from the sample holder contribution. The core diamagnetism was calculated using tabulated Pascal increments.[19] A contribution χ_{dia} of, respectively, -3.48×10^{-4} and -3.49×10^{-4} cm^3/mole was subtracted from the measured data of $Ga_{0.87}Ti_4S_8$ and GaV_4S_8, respectively.

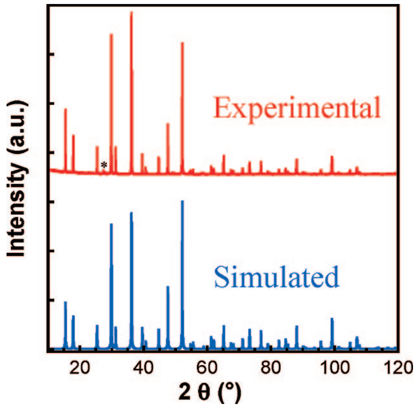

Figure 1. X-ray powder diffraction pattern of $Ga_{0.87}Ti_4S_8$ (top curve). The impurity peaks of Ga_2S_3 are indicated by *. This experimental powder pattern agrees well with the simulated pattern obtained using the structure as solved from the single-crystal study (bottom curve).

3. Results and Discussion

The AM_4X_8 (with A = Ga, Ge; M = V, Nb, Ta, Mo; X = S, Se) family of compounds exhibits a remarkable structure where the tetrahedral transition metal clusters can accommodate a wide range of valence electron count (VEC). The VEC of the M_4 cluster is indeed as low as 7 in the vanadium compound GaV_4S_8 and can reach 11 in the molybdenum compound $GaMo_4S_8$.[10,11] So far, the synthesis of AM_4X_8 compounds with cluster VEC lower than 7 was never reported in the literature. Reducing the VEC of the cluster could strongly impact on the metal−metal bonding and affect the physical properties of the compound. We have therefore started the synthesis of the unknown $GaTi_4S_8$ compound that would contain only 3 electrons per cluster (VEC = 3). In that purpose, a stoichiometric mixture of Ga_2S_3, Ti, and S was heated at high temperature as described in the experimental section. This synthesis led to a black powder sample whose X-ray diffraction pattern (see Figure 1) revealed the presence of Ga_2S_3 as a side product beside a majority of peaks that gave no hint of known phase recorded in the standard JCPDF database. Single crystals of this phase (tetrahedrons or cubes with 300 μm edge length) were subsequently obtained from iodide vapor transport method. Chemical analysis of the crystals revealed a composition $Ga_{0.78(2)}Ti_{4.00(1)}S_{7.94(2)}$, suggesting a slight deficiency of Gallium compared to targeted composition $Ga_1Ti_4S_8$.

The structure was solved by means of X-ray diffraction as described in the Experimental Section (see Tables 1 and 2 for details). The refinement revealed that the title compound adopts a deficient spinel type structure and confirmed the slight Ga non stoichiometry. This led to a refined chemical formula $Ga_{0.87(1)}Ti_4S_8$ in good agreement with the analyzed one $Ga_{0.78(2)}Ti_{4.00(1)}S_{7.94(2)}$. Figure 2 represents the structure of the deficient spinel compound $Ga_{0.87}Ti_4S_8$ with view along

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[18] Kraus, W.; Nolze, G. *PowderCell for Windows 2.4*; FIMRT: Berlin, 2000.

[19] König, E. and König G. *Magnetic Properties of Coordination and Organometallic Transition Metal Compounds*; Springer-Verlag: Berlin, 1974.

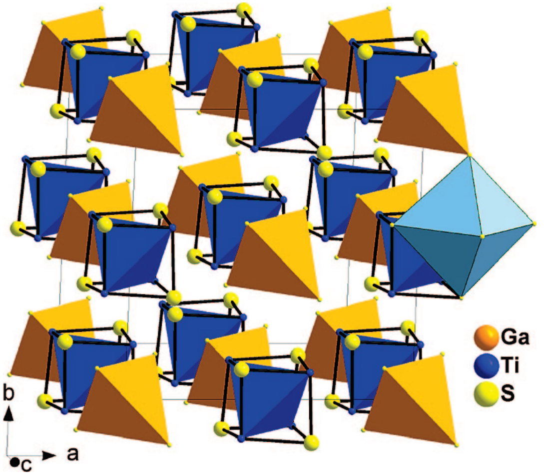

Figure 2. Crystallographic structure of $Ga_{0.87}Ti_4S_8$. The rock-salt-like distributions of GaS_4 tetrahedra (orange) and Ti_4 tetrahedral clusters (dark blue) are emphasized. The TiS_6 octahedron (light blue) and the Ti_4S_4 cubanelike arrangements are also represented.

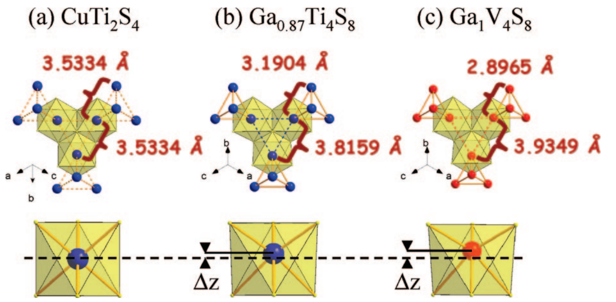

Figure 3. Metal−metal bonding and shift along the [111] direction of the transition metal atom within its sulfur octahedral site (a) in the regular spinel $CuTi_2S_4$ showing no clustering, (b) in $Ga_{0.87}Ti_4S_8$ showing a partial clustering, and (c) in GaV_4S_8 showing tetrahedral clusters.

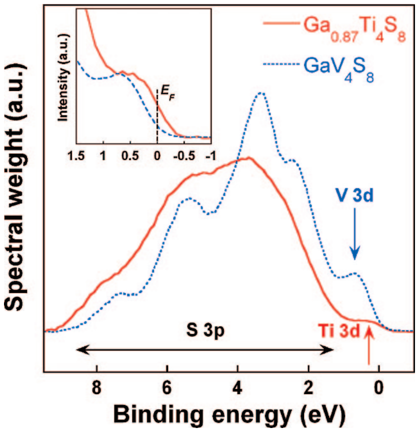

Figure 4. XPS measurement of the valence bands of $Ga_{0.87}Ti_4S_8$ and GaV_4S_8 single crystals normalized to S 3p spectral weight and to the maximum of the M 3d (M = Ti, V) band (inset). The background was substracted before normalization.

the *a* direction. In this compound also we observed a shift of the Ti atom off the center of the chalcogen octahedra. Consequently, they form tetrahedral Ti_4 clusters characterized by metal−metal distances $d_{M-M} = 3.1904(8)$ Å, separated each other by long Ti−Ti distances $d_{M---M} = 3.8158(8)$ Å. A major issue in this compound concerns the degree of clustering compared to other members of the family. Figure 3 compares the local transition metal coordination in the regular spinel $CuTi_2S_4$,[20] with the deficient spinels $Ga_{0.87}Ti_4S_8$ and GaV_4S_8. At first glance, the shift of the transition metal atoms M off the centers of the chalcogenide octahedral site in $Ga_{0.87}Ti_4S_8$ seems intermediate between the fully clusterized compound GaV_4S_8 and the cluster free spinel $CuTi_2S_4$. To quantify the distortion of the structure from ideal spinel two parameters are interesting to study:[8] the degree of clustering of the transition metals M (defined like $D^{MM} = ((d_{M---M}/d_{M-M}) - 1)x\ 100(\%))$, and the degree of distortion of the transition metal coordination from the ideal octahedral coordination (defined like $D^{MQ} = ((d_{M-Q2}/d_{M-Q1}) - 1)x\ 100(\%))$. Interestingly, both parameters are significantly lower in $Ga_{0.87}Ti_4S_8$ ($D^{MM} = 19.6\%$, $D^{MQ} = 6.1\%$) than in other deficient spinel compounds GaM_4X_8 (M = V, Nb, Ta, Mo; X = S, Se) where $D^{MM} \approx 40\%$ and $D^{MQ} \approx 10\%$. It clearly shows that in $Ga_{0.87}Ti_4S_8$ the transition metal atoms are less clusterized and the octahedral coordination less distorted than in other known deficient spinels. This declustering is likely associated to the decrease of the electronic filling of the clusters in $Ga_{0.87}Ti_4S_8$ (~3 electrons) compared to other members of the family that contains from 7 to 11 electrons per clusters. Band structure calculations have shown indeed that all the occupied molecular orbital of the M_4 cluster have a M−M bonding character in AM_4X_8 compounds.[10] A smaller number of electrons per cluster should thus result in a weaker intracluster M-M bond and subsequently a lowering of D^{MM} and D^{MQ} as observed in $Ga_{0.87}Ti_4S_8$. These structural features are of special interest as they were found to tune the pressure induced insulator to metal transition in the GaM_4X_8 (M = Nb, Ta; X = S, Se) compounds.[8] This urges us to explore the physical properties of the new thiospinel compound $Ga_{0.87}Ti_4S_8$.

Figure 4 shows the valence bands of $Ga_{0.87}Ti_4S_8$ and GaV_4S_8 measured by X-ray Photoemission Spectroscopy. First, we observe notable differences in the S 3p bands located between E_B = 1.5 and 9 eV, with four narrow structures in GaV_4S_8 and almost featureless shoulderlike structures in $Ga_{0.87}Ti_4S_8$. The narrow structures observed in GaV_4S_8 indicate the presence of peaks in the density of state (DOS) which means a small band dispersion due to weak intercluster transfer integrals *t*. Conversely, the featureless shoulder-like structures observed in $Ga_{0.87}Ti_4S_8$ supports a strengthening of the intercluster transfer integrals *t* (i.e., a stronger band dispersion) mediated by the sulfur ions. This is consistent with the result of the crystal structure analysis showing a slackening of these clusters and a decrease of the distortion of TiS_6 octahedra both features impacting on the transfer integrals.[8] As expected, we also found a clear variation of the transition metal 3d spectral weight between GaV_4S_8 and $Ga_{0.87}Ti_4S_8$, which is a consequence of the larger 3d electron density per cluster in GaV_4S_8 compared to $Ga_{0.87}Ti_4S_8$ (7 and ~3 electrons respectively). Interestingly, the inset of Figure 4 shows that a gap (0.2 ± 0.1 eV) appears below the Fermi level in GaV_4S_8. This result is consistent with the band structure calculations (LDA+U) performed for this compound,[12] and to our knowledge, it is the first direct experimental evidence supporting that this compound is really a Mott insulator. Conversely, a finite spectral weight

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(20) Okada, H.; Koyama, K.; Watanabe, K. *J. Alloys Compd.* **2005**, *403*, 34–37.

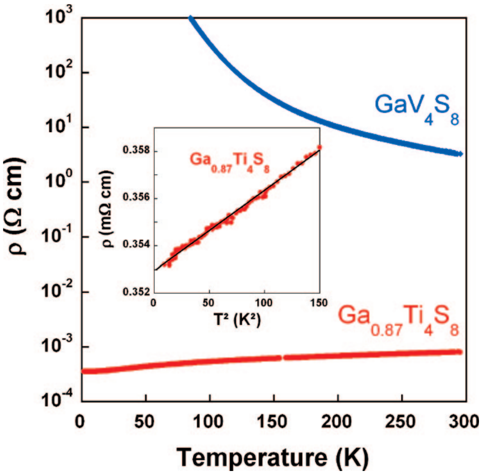

Figure 5. Temperature (T) dependence of the resistivity (ρ) of $Ga_{0.87}Ti_4S_8$ and GaV_4S_8. The inset shows the low temperature resistivity plotted vs T^2.

exists at the Fermi level in $Ga_{0.87}Ti_4S_8$, which strongly suggests that this compound is a metal with a Fermi step.

In agreement with these spectroscopic measurements, the temperature dependence of the resistivity of $Ga_{0.87}Ti_4S_8$ crystals shows a positive temperature coefficient consistent with a metallic like behavior (see Figure 5). This contrasts with the semiconducting behavior measured on pressed pellets of the Mott insulator GaV_4S_8,[10] and on our crystals of this compounds (see Figure 5). The resistivity value of $Ga_{0.87}Ti_4S_8$ at 300K is 8×10^{-4} Ω.cm which is higher than the value (3×10^{-4} Ω cm) found in the regular metallic spinel $CuTi_2S_4$.[20] It is worth noting that the resistivity below 12 K is well characterized by the relation $\rho = \rho_o + AT^2$, with $\rho_o \approx 0.35$ mΩ cm and $A = 0.033$ μΩ cm K^{-2}. This quadratic dependence at low temperature, expected in the Fermi liquid model, suggests that the electron–electron scattering dominates the electron–phonon scattering process at low temperature. Moreover, the residual resistivity ratio (RRR = 2.3) is very small in $Ga_{0.87}Ti_4S_8$ compared to value reported for the metallic compound $CuTi_2S_4$ (RRR = 21.2).[20] Such low RRR values are typically observed in doped Mott insulators close to a metal–insulator transition, which exhibit a correlated metal type behavior.[14]

To get more insight into this possible correlated character of the metallic state in $Ga_{0.87}Ti_4S_8$, we also measured its specific heat and magnetic susceptibility. The low temperature specific heat C of $Ga_{0.87}Ti_4S_8$, plotted as C/T vs T^2, is shown in Figure 6. Data below 12 K are very well described by $C/T = \beta T^2 + \gamma$. The first term represents the phonon contribution; the value of β given by the fit is $7.44.10^{-4}$ J K^{-4} mol^{-1}, which corresponds to a Debye temperature θ_D of 340 K. This is very close to $\theta_D = 352$ K measured in the related spinel compound $CuTi_2S_4$.[20] The second term, the Sommerfeld constant γ, corresponds to the electronic specific heat expected in a metal and is related to the density of states $N(E_F)$ according to $\gamma = (2/3)\pi^2 k_B{}^2 N(E_F)$. In $Ga_{0.87}Ti_4S_8$ γ reaches 58 mJ K^{-2} mol^{-1} (or equivalently 29 mJ K^{-2} $(Ga_{0.435}Ti_2S_4\ mol)^{-1}$), which corresponds to a density of states $N(E_F) = 12.3$ states eV^{-1} (formula unit)$^{-1}$ (or equivalently to 3.07 states eV^{-1} (Ti atoms)$^{-1}$). This is comparable to the value reported in $CuTi_2S_4$ ($\gamma = 23.9$ mJ K^{-2} mol^{-1}).[20] Interestingly, the electronic specific heat measured in $Ga_{0.87}Ti_4S_8$ and in $CuTi_2S_4$ widely exceeds the values observed in conventional uncorrelated metals (γ is, for example, 0.7 mJ/K²/mol in copper),[21] but are comparable to the values reported in doped Mott insulators (γ is in the 10–20 mJ K^{-2} mol^{-1} range in slightly doped $LaTiO_3$).[22]

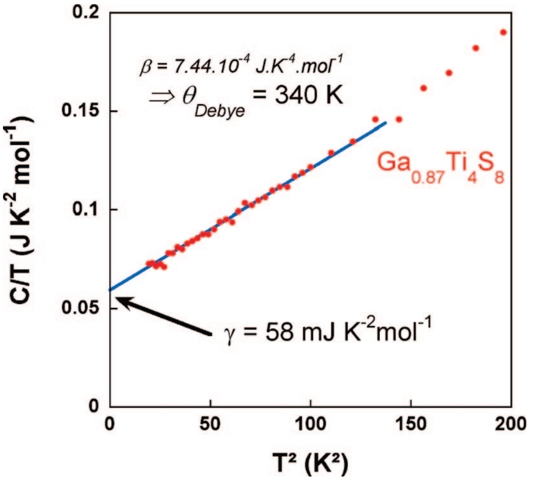

Figure 6. Low-temperature specific heat C of $Ga_{0.87}Ti_4S_8$ plotted as C/T vs T^2.

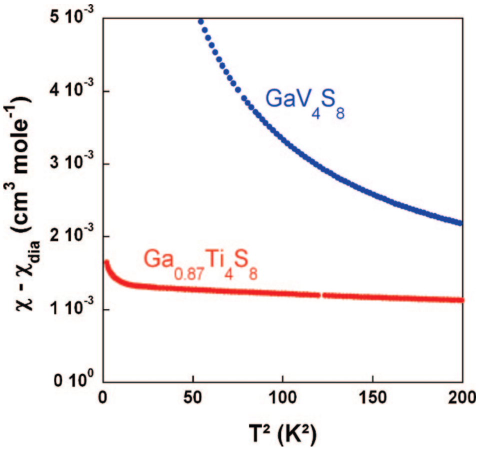

Figure 7. Magnetic susceptibility of $Ga_{0.87}Ti_4S_8$ and GaV_4S_8. The core diamagnetic contribution was subtracted from the measured data.

Figure 7 represents the molar magnetic susceptibility of $Ga_{0.87}Ti_4S_8$. No difference was observed between ZFC and FC measurements. The magnetic susceptibility is rather constant between 300 and 15 K and increases rapidly at lower temperatures, probably because of the presence of a small amount of paramagnetic impurities. The almost temperature-independent susceptibility above 15 K is reminiscent of the Pauli paramagnetic susceptibility observed in metals. It strongly contrasts with the magnetic susceptibility measured for the isostructural Mott insulator GaV_4S_8 also shown in Figure 7. As discussed in previous work,[10] GaV_4S_8 presents a Curie–Weiss behavior corresponding to one unpaired electron per V_4 cluster. This is consistent with the electronic

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(21) Osborne, D. W.; Flotow, H. E.; Schreiner, F. *Rev. Sci. Instrum.* **1967**, *38*, 159.

(22) Tokura, Y.; Taguchi, Y.; Okada, Y.; Fujishima, Y.; Arima, T.; Kumagai, K.; Iye, Y. *Phys. Rev. Lett.* **1993**, *70*, 2126.

structure calculated for the $\mathrm{V_4}$ cluster containing 7 electrons distributed on the (a_1),[2] (e),[4] and (t_2)[1] orbital as represented in Figure 7.[10] Interestingly, we can expect ∼3 electrons per $\mathrm{Ti_4}$ cluster in $\mathrm{Ga_{0.87}Ti_4S_8}$, which should also lead to one unpaired electron per cluster as shown in Figure 7. The susceptibility of $\mathrm{Ga_{0.87}Ti_4S_8}$ is not consistent with the presence of almost one unpaired electron localized per $\mathrm{Ti_4}$ cluster and resembles more that of the metallic spinel $\mathrm{CuTi_2S_4}$.[20] The low-temperature magnetic susceptibility of $\mathrm{Ga_{0.87}Ti_4S_8}$ can be well-described by $\chi = \chi_P + C/(T - \theta)$, where χ_P represents the Pauli susceptibility expected for a metal and the second term accounts for the low temperature Curie-like increase. The latter corresponds to less than 0.15% of spin $s = ½$ per Ti ion and is therefore likely due to a small amount of paramagnetic impurities. The Pauli paramagnetic susceptibility χ_p is equal to 1.25×10^{-3} cm^3/mol for $\mathrm{Ga_{0.87}Ti_4S_8}$, which is equivalent to 6.25×10^{-4} cm^3/($\mathrm{Ga_{0.435}Ti_2S_4}$ mol). This is is again larger than $\chi_P = 5.4 \times 10^{-4}$ cm^3/mol reported for $\mathrm{CuTi_2S_4}$.

Interestingly, the Wilson ratio ($R_W = \chi_P/\gamma$ in the units of $3\,\mu_B{}^2/\pi^2 k_B{}^2$) reaches 1.57 in $\mathrm{Ga_{0.87}Ti_4S_8}$, which is unambiguously larger than $R_W = 1$ expected for noninteracting metallic systems. Such an enhanced Wilson ratio is predicted for strongly correlated doped Mott insulators, as indicated by the dynamical mean-field theory.[23] This "doped Mott insulator" scenario also explains the rather low residual resistivity ratio observed in $\mathrm{Ga_{0.87}Ti_4S_8}$. Another benchmark used to evaluate the correlated character of a metal is the Kadowaki-Woods ratio, which is defined as the ratio between the prequadratic term (A) of the resistivity and the square of the Sommerfeld constant (γ^2).[24] In $\mathrm{Ga_{0.87}Ti_4S_8}$, the Kadowaki-Woods ratio A/γ^2 reaches 9.8×10^{-6} $\mu\Omega$ cm (mol K^2/mJ)^2, which is very close to the universal value 1×10^{-5} $\mu\Omega$ cm (mol K^2/mJ)^2, observed in strongly correlated metals and far above the 4.10^{-7} $\mu\Omega$ cm (mol K/mJ), of the weakly correlated metals. Therefore, all the physical properties measured for $\mathrm{Ga_{0.87}Ti_4S_8}$, i.e., XPS valence band, resistivity, specific heat and magnetic susceptibility, show that this compound is a metal with signs of electronic correlations. Most probably $\mathrm{Ga_{0.87}Ti_4S_8}$ is a doped Mott insulator in the vicinity of the metal–insulator transition. Following this idea, the stoichiometric compound $\mathrm{Ga_1Ti_4S_8}$ would be interesting to study as it would be even closer to the Mott insulating state. So far, all our efforts to synthesized this compound failed.

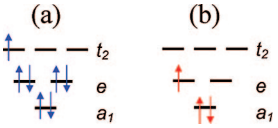

Figure 8. Electronic structure of the tetrahedral transition metal cluster (a) calculated in ref 10 for a $\mathrm{V_4}$ cluster in $\mathrm{GaV_4S_8}$, and (b) expected for a $\mathrm{Ti_4}$ cluster in the hypothetical compound $\mathrm{GaTi_4S_8}$.

Conclusion

We have synthesized and characterized the first Ti member of the $\mathrm{AM_4X_8}$ family of tetrahedral transition metal cluster compounds with deficient spinel type structure. The single-crystal X-ray structure determination of $\mathrm{Ga_{0.87}Ti_4S_8}$ revealed the presence of Ga vacancies and a partial declustering of the transition metal atoms compared to other members of the family. This declustering is likely associated to the decrease of the electronic filling of the clusters in $\mathrm{Ga_{0.87}Ti_4S_8}$ (∼3 electrons) compared to other $\mathrm{AM_4X_8}$ compounds that contains from 7 to 11 electrons per clusters. XPS measurements shows that the valence band of $\mathrm{Ga_{0.87}Ti_4S_8}$ is more dispersed than that of the Mott insulator $\mathrm{GaV_4S_8}$. this suggests a strengthening of the transfer integrals induced by the slackening of the transition metal clusters. Moreover, $\mathrm{Ga_{0.87}Ti_4S_8}$ shows a Fermi step that is consistent with a metallic character whereas a gap appears (0.2 eV) below the Fermi level in the Mott insulator $\mathrm{GaV_4S_8}$. The resistivity, specific heat, and magnetic susceptibility of $\mathrm{Ga_{0.87}Ti_4S_8}$ demonstrate that this compound is a metal which contrast with the paramagnetic Mott insulating state observed in other members of the family. Finally, the RRR, Wilson and Kadowaki-Woods ratios strongly support that $\mathrm{Ga_{0.87}Ti_4S_8}$ behaves as a correlated metal.

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Supporting Information Available: Crystallographic information file (CIF) of $\mathrm{Ga_{0.87}Ti_4S_8}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(23) Georges, A.; Kotliar, G.; Krauth, W.; Rozenberg, M. J. *Rev. Mod. Phys.* **1996**, *68*, 13–125.

(24) Kadowaki, K.; Woods, S. B. *Solid State Commun.* **1986**, *58*, 507–509.