Physical and optical properties of the quaternary sulfides $SrCu_2MS_4$ and $EuCu_2MS_4$ (M = Ge and Sn)

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Abstract

Four quaternary sulfides $SrCu_2MS_4$ and $EuCu_2MS_4$ (M = Ge and Sn) were prepared from a thoroughly ground mixture of EuS or SrS, Cu, or Sn, and S in stoichiometric proportions. Electrical conductivity measurements on pressed pellets showed that all the phases are semiconductors. The optical band gaps were assessed at 2.8 eV for $SrCu_2GeS_4$, 2.1 eV for $SrCu_2SnS_4$, 2.2 eV for $EuCu_2SnS_4$, and 1.6 eV for $EuCu_2GeS_4$. Both Sr-based compounds present a temperature-independent paramagnetism, of about $+135 \times 10^{-6}$ and $+92 \times 10^{-6}$ emu/mol, for $SrCu_2SnS_4$ and $SrCu_2GeS_4$, respectively. In the case of the europium compounds, they follow a Curie–Weiss dependence above 1.8 K ($EuCu_2GeS_4$) and above 4 K (for $EuCu_2SnS_4$), with values of the magnetic effective moment μ_{eff} and the Curie–Weiss temperature Θ, equal to 6.27 μ_B and -2.8 K for $EuCu_2GeS_4$, and 6.81 μ_B and $+0.7$ K, for $EuCu_2SnS_4$. The experimental magnetic moments confirm that the europium ion is in divalent state, similar to Sr in the related compounds.

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1. Introduction

The chemistry of ternary and quaternary germanium and tin chalcogenides has been extensively studied in the last decade. Many alkaline-earth and rare-earth ternary germanium and tin sulfides have been reported [1–5]. Quaternary tin and germanium sulfides were reported the first time by Ch. Teske in 1976 [6], and recently Johrendt and Kanatzidis [7,8] have systematically studied complex sulfides of transition metals and XIV group elements. These studies include, for example, the synthesis and characterization of compounds such as $Rb_2Cu_2SnS_4$, $Na_2Cu_2Sn_2S_6$, and $BaCu_6Ge_2S_8$.

The interest in these compounds is based on their potential applications in nonlinear optics phenomena, optical storages, solar energy conversion, and catalysis [9–12].

The investigation in our laboratory of the quaternary rare-earth transition metal chalcogenides led us to the synthesis of two new phases $EuCu_2SnS_4$ and $EuCu_2GeS_4$, which are isostructural with the analog Ba and Sr-containing sulfides previously described by Teske [6].

The crystal structure of these phases can be schematically described as a three-dimensional framework of corner sharing $[CuS_4]^{-7}$, and $[MS_4]^{-4}$ (M = Sn, Ge) tetrahedra. The divalent ions are in eightfold coordination forming a distorted cubic antiprism polyhedron.

According to the usual electron counting rules, that implies the following Sr (+II) and Eu (+II), Cu (+I), Sn (+IV) and Ge (+IV) oxidation states, and from the color of the series of compounds (green for the germanium sulfides, and the reddish brown for the tin sulfides), it is possible to predict a semi-conducting behavior for all these compounds, with an absorption band in the visible part of the optical spectrum. These predictions, however, have not been demonstrated experimentally, because neither the electrical nor the magnetic properties have been investigated.

In the present paper, we have undertaken an investigation of the electrical and magnetic properties

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as well as some of the optical properties of these family of compounds, in particular the diffuse reflectance measurements for the sulfides of formula $SrCu_2MS_4$ or $EuCu_2MS_4$ (M = Sn, Ge).

2. Experimental

Polycrystallines $SrCu_2MS_4$ and $EuCu_2MS_4$ (M = Ge, Sn) phases were prepared from a thoroughly ground mixture of EuS or SrS, Cu (Aldrich, 99.5% pure), Ge (Aldrich, 99.99% pure) or Sn (Aldrich, 99.8% pure), and S (Aldrich, 99.5% pure) in stoichiometric proportions. The mixtures were placed in an alumina boat and heated in a CS_2/Ar stream at 723 K for about 36 h, with two intermittent grindings. All phases are colored: $SrCu_2GeS_4$ and $EuCu_2GeS_4$, green, and $SrCu_2SnS_4$ and $EuCu_2SnS_4$, reddish brown, and stable in air.

The SrS and EuS were prepared by heating $SrCO_3$ (Aldrich, 99.995% pure) or Eu_2O_3 (Aldrich, 99.99% pure), respectively, in an alumina crucible at 900 K, under continuous flow of CS_2/Ar.

To check phase purity, powder X-ray diffraction (PXD) data were collected with a Siemens D-5000 difractometer fitted with a graphite monochromator, using $CuK\alpha$ radiation ($\lambda = 154.057$ pm), with quartz as internal standard. The experimental powder patterns were almost in perfect agreement with those calculated from the single-crystal data using the program Lazy-Pulverix [13]. First inspection of the powder pattern revealed a close relationship between all phases.

The electrical conductivity measurements were carried by using the electrochemical impedance spectroscopy (EIS) technique from room temperature to 450 K. A VoltaLab40 PGZ301 universal potentiostat was used for all measurements. The applied signal amplitude was 10 mV in the 10 Hz to 1 kHz frequency range. Cylindrical pellets (area = 0.29 cm², and thickness between 0.05 and 0.15 cm) were made from pressed powders of $SrCu_2MS_4$ and $EuCu_2MS_4$. Impedance measurements were made in a conductivity cell provided with two identical electrodes. The two opposite flat surfaces of the samples were covered with gold by sputtering and sandwiched between the gold electrodes of the conductivity cell.

Diffuse reflectance spectra were recorded in order to determine the gap between the valence and conduction bands. A Perkin-Elmer Lambda 20 UV/Vis spectrophotometer equipped with a Labsphere RSA-PE-20 diffuse reflectance accessory was used to measure the diffuse reflectance spectra of $SrCu_2MS_4$ and $EuCu_2MS_4$ over the range 200 nm (6.2 eV) to 600 nm (2.1 eV). The samples were ground into powder and pressed to form a very thin layer onto MgO on a sample holder. MgO pressed powder was used as reference.

The magnetic measurements were performed on a SHE-VTS-906 SQUID magnetometer, from 2 K up to room temperature, under a static field of 1 kOe (Eu-based samples) or 5 kOe (Sr-based compounds). The powdered samples were contained in gelatin capsules whose contributions were subtracted at each temperature point.

3. Results and discussion

The least-squares refinements (trigonal cell) of the PXD patterns yielded the unit-cell parameters, which are presented in Table 1 along with the previously reported unit-cell parameters for $SrCu_2SnS_4$ and $SrCu_2GeS_4$. Whereas $SrCu_2SnS_4$ and $EuCu_2SnS_4$ crystallize in the space group $P3_1$ (No. 144), the space group of the Ge-derivatives is $P3_2$ (No. 145) [6–14]. Latter studies suggest that the appropriate space group for this type of compounds is $P3_221$ (No. 154) or its enantiomer $P3_121$ (No. 153) [15].

The curves $\log \sigma = f(T)$ illustrated in Fig. 1 for $EuCu_2GeS_4$ (curve 1), $SrCu_2GeS_4$ (curve 2), $SrCu_2SnS_4$ (curve 3), and $EuCu_2SnS_4$ (curve 4) in the temperature range 293–450 K are typical for semi-conducting materials. The room temperature resistivities and activation energy values are shown in Table 1. All these values are typical for this type of conduction.

The UV-Vis spectra of all compounds presented here show a very strong absorption band in the wave-number range 450–800 nm from which the optical band gap can be derived (Fig. 2). The optical band gap corresponds to the intersection point between the base line along the energy axis and the extrapolated line from the linear portion of the spectrum. With these data, the band gaps E_g can be assessed at 2.8 eV for $SrCu_2GeS_4$, 2.1 eV for $SrCu_2SnS_4$, 2.2 eV for $EuCu_2SnS_4$, and 1.6 eV for $EuCu_2GeS_4$. The E_g values are consistent with the citreous color of $SrCu_2GeS_4$, the green color of the $EuCu_2GeS_4$ and the red-brown color of the Sn-derivatives.

Noticeable is that the band gap of $EuCu_2GeS_4$ (1.6 eV) is relatively small and comparable to those of $CuInS_2$ (1.55 eV) or the related phase $Rb_2Cu_2Sn_2S_6$ (1.44 eV). These values suggest that this compound is suitable for efficient absorption of most of the solar radiation making it potential candidate for solar cell applications [8].

The Sr-based compounds present both a diamagnetic signal of about -80×10^{-6} and -105×10^{-6} emu/mol at 300 K, for $SrCu_2SnS_4$ and $SrCu_2GeS_4$, respectively. After subtraction of the diamagnetic contributions of the constituent atoms [16], the respective room temperature magnetic susceptibilities amount to $+135 \times 10^{-6}$ and $+92 \times 10^{-6}$ emu/mol. These values were used for the analysis of the magnetic susceptibility

Table 1
Unit-cell parameters and the electrical, optical and magnetic properties of $SrCu_2MS_4$ and $EuCu_2MS_4$ ($M = Ge$ and Sn)

Compound	a (Å)	c (Å)	ρ (RT) (Ω cm)	E_a (eV)	E_g (eV)	θ (K)	μ_{eff} (MB)
$EuCu_2GeS_4$	6.102(3)	15.22(8)	24.21	0.79	1.6	−2.7	6.27
$EuCu_2SnS_4$	6.249(8)	15.48(7)	862.1	0.94	2.2	0.7	6.81
$SrCu_2GeS_4$	6.143(2)	15.282(6)	403.2	1.75	2.8	TIP	—
$SrCu_2SnS_4$	6.268(2)	15.533(4)	27.10	1.04	2.1	TIP	—

TIP: temperature-independent paramagnetism.
The unit-cell parameter for $SrCu_2GeS_4$ and $SrCu_2SnS_4$ were taken from the literature [6,14] and for $EuCu_2GeS_4$ and $EuCu_2SnS_4$ were obtained from this work.
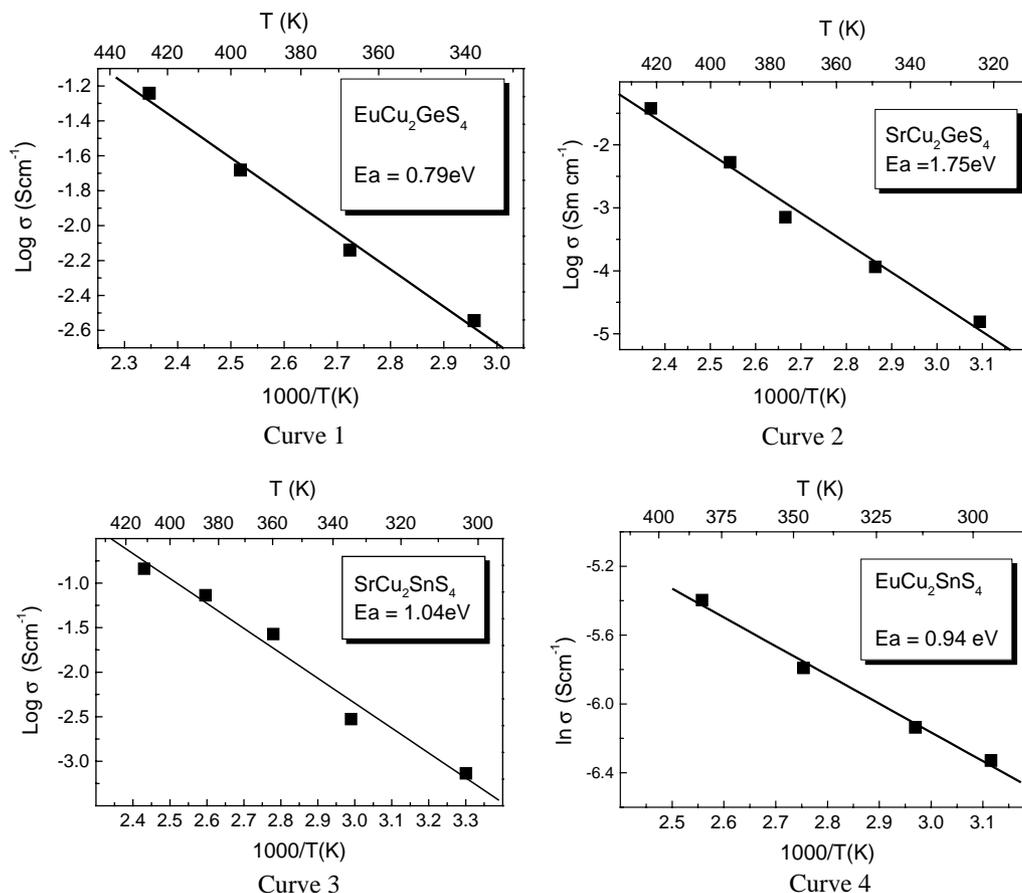
Fig. 1. Electrical conductivity as a function of temperature.

of the Eu-based compounds, by subtracting the bare susceptibility of the $SrCu_2SnS_4$ from the $EuCu_2SnS_4$ data and, similarly, $SrCu_2GeS_4$ from that of $EuCu_2GeS_4$. Fig. 3 shows the corrected data of the inverse susceptibility of $EuCu_2SnS_4$ and $EuCu_2GeS_4$, measured after zero-field cooling. Assuming a Curie–Weiss dependence in the paramagnetic state, these data were fitted by a least-squares refinement in the temperature range 1.8–300 K for $EuCu_2GeS_4$, and 4–300 K for $EuCu_2SnS_4$. The obtained values of the magnetic effective moment μ_{eff} and the Curie–Weiss temperature Θ were equal to $6.27(\pm 0.10)\,\mu_B$ and $-2.8(\pm 0.2)$ K for $EuCu_2GeS_4$, and $6.81(\pm 0.05)\,\mu_B$ and $+0.7(\pm 0.1)$ K for $EuCu_2SnS_4$.

The experimental magnetic moments are lower than the one expected for a Eu^{2+} free ion (7.94 μ_B), but much higher than an eventual van Vleck contribution due to the admixture of the $^7F_0$ and $^7F_1$ levels of the Eu^{3+} ion (experimental moments of 3.2–3.6 μ_B [17,18]). We may confirm then, that europium is at its 2+ oxidation state, similar to Sr in the isostructural compounds.

At low temperatures, the magnetic behavior of the Eu-based samples differs from one compound to the other (inset of Fig. 3). While $EuCu_2GeS_4$ follows a Curie–Weiss dependence down to our lower experimental temperature, extrapolating to $\Theta = -2.8(\pm 0.2)$ K, $EuCu_2SnS_4$ shows a ferromagnetic-like behavior: its
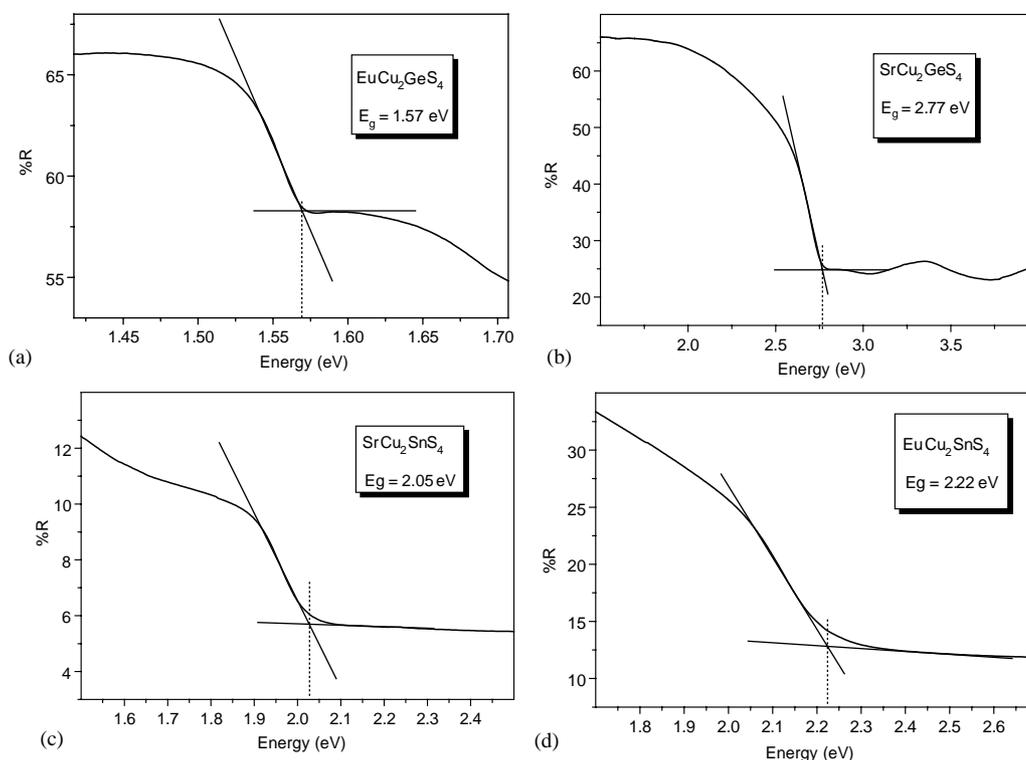
Fig. 2. Diffuse reflectance spectra of (a) $EuCu_2GeS_4$, (b) $SrCu_2GeS_4$, (c) $SrCu_2SnS_4$, and (d) $EuCu_2SnS_4$ ($T = 300\,K$).
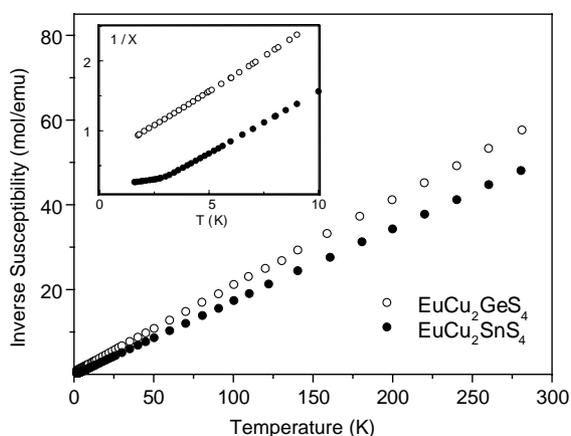
Fig. 3. Inverse molar susceptibility of $EuCu_2GeS_4$ and $EuCu_2SnS_4$, measured under an applied field of 1 kOe. The inset zooms the low-temperature data.

susceptibility levels off at about 3 K, while the data extrapolates to $\Theta = +0.7(\pm 0.1)\,K$.

It becomes difficult to ascribe the low magnetic moments to stoichiometric effects or to a mixture of oxidation states for the europium ion. The presence of Eu^{3+} should lead to a non-linear $\chi^{-1}(T)$ behavior, in disagreement with the very small esd's observed experimentally. A possibility may come from a "dynamic" mixed-valence state, as observed in some Sm-based compounds [19–21]. However, the europium ion has never shown such effects, to our knowledge, because

of the well-isolated $^8S_{7/2}$ ground state and no intrinsic effects should be expected. The striking difference in these magnetic behaviors should be investigated deeper, either by magnetic data at very low temperature (millikelvin region) or by neutron diffraction in samples fabricated from a specific europium isotope (^{153}Eu). Small differences in the interatomic distances and/or angles may be responsible of the existence of such ferromagnetic exchange interactions.

Acknowledgments

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