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Thermodynamic Properties of $RZnSn_2$ (R = Y, Er, Lu) Compounds with $HfCuSi_2$ Structure Type

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Abstract. The results of magnetic and specific heat studies are reviewed and discussed for the series of $RZnSn_2$ (R = Y, Er and Lu) compounds crystallizing in the same tetragonal $HfCuSi_2$-type of structure. A sharp peak in the specific heat of $ErZnSn_2$ compound is indicative for magnetic ordering of Er moments at 5.0 K, being in agreement with its established antiferromagnetic nature. The estimated magnetic entropy S_{magn} contribution is less than that expected for the ground state J = 15/2 multiplet of Er^{3+}.

Introduction

The new ternary intermetallic compounds $RZnSn_2$ (R = Y, Gd, Tb, Dy, Ho, Er, Tm, Lu) have been recently synthesized. It was shown that they crystallize in the tetragonal $HfCuSi_2$ structure type [1]. These stannides belong to the rich family of R-T-X intermetallics, which present a variety of crystal and magnetic structures and a plethora of interesting physical properties, including magnetism, superconductivity and intermediate valency. Since Zn and Sn atoms do not carry magnetic moments themselves, magnetic properties of $RZnSn_2$ compounds are governed by the rare earth moments, by their conduction - electron mediated exchange interactions, and by the effects of crystalline electric fields (CEF) acting on the 4f states. Hence, the knowledge of CEF effects is of special interest. Especially, for a quantitative interpretation of the temperature dependence of the specific heat and of the entropy the knowledge of the actual level scheme, i.e., of the CEF parameters is needed, but no experimental results concerning this issue have been published so far for the $RZnSn_2$ series.

The aim of this work is to present and discuss some of preliminary magnetic and specific heat data measured within wide temperature range by means of PPMS for three $RZnSn_2$ (R = Y, Er, and Lu) intermetallics.

Experimental

The polycrystalline $RZnSn_2$ (R = Y, Er and Lu) samples have been prepared as described previously [1] and their crystal structures were determined from powder diffractograms using the FullProf program [2] for Rietveld refinements.

The bulk magnetic and specific heat measurements were performed in the temperature range 1.9 K - 300 K by means of the vibrating sample magnetometer (VSM) and the heat capacity (HC) options of the Quantum Design physical property measurement system (PPMS). The reported here specific heat studies were made in zero external magnetic field. Special care was taken to correct in a proper way the raw HC results taking into account of the specific heat contribution originating from the adhesive addenda (*Apiezon N*) that is used to couple a given sample to the PPMS HC platform.

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Experimental results and discussion

X-ray diffraction analysis showed that all the investigated compounds crystallize with the $HfCuSi_2$-type structure, space group *P4/nmm* [1].

Among the studied compounds only $ErZnSn_2$ exhibits a clear paramagnetic to antiferromagnetic phase transition in the experimental temperature range at T_N = 5.0 K [1]. The antifferomagnetic character of this compound correlates with its negative paramagnetic Curie temperatures θ_P = -8.8 K and a metamagnetic behaviour of its magnetization curve recorded at the lowest temperatures [1]. The observed increase of mass magnetic susceptibility $\chi_\sigma(T)$ dependence below T_N (Fig. 1) could signalize another phase transition at lower temperature (out of experimental range), but most probably induced by the moments reorientation in magnetic field used (H = 1000 Oe), since this behavior is absent in the data taken at H = 50 Oe [1]. The derived magnetic effective moment, μ_{eff} = 10.47·μ_B, is higher than the expected theoretical value for the Er^{3+} free-ion value ($\mu_{eff}(theor.) = g\mu_B[J(J+1)]^{1/2}$ = 9.58 μ_B) and a possible reason for the observed excess has already been discussed [1], being tentatively related, at least in part, to the contribution originated from the delocalized *d*-electrons of Zn. Especially, similar excess of magnetic effective moment is well established for ternary Gd-T-X compounds [3-12], but in this case the main contribution to the excess arises from the Gd 5*d* electrons and it is induced via 4*f*-5*d* exchange interactions, while the contribution coming from the conduction *d* electrons of a given T-element plays a secondary role.

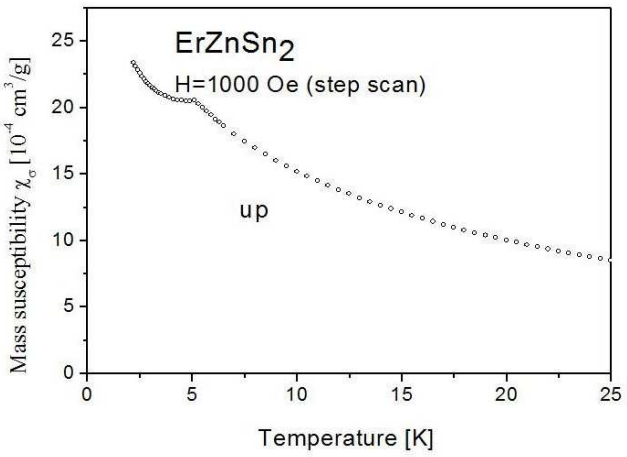

Fig. 1. Temperature dependence of the magnetic susceptibility for $ErZnSn_2$, measured with rising temperature in an H = 1000 Oe external magnetic field. The anomaly points to an antiferromagnetic transition, agreeing with previous low field ZFC data (Fig. 8b in ref. [1]).

The specific heat results are shown in Figs. 2a and 2b for all title compounds. Among them only $ErZnSn_2$ shows a sharp λ type anomaly at T_N = 5.0 K, being exactly as the Néel temperature obtained from the low field magnetic measurements.

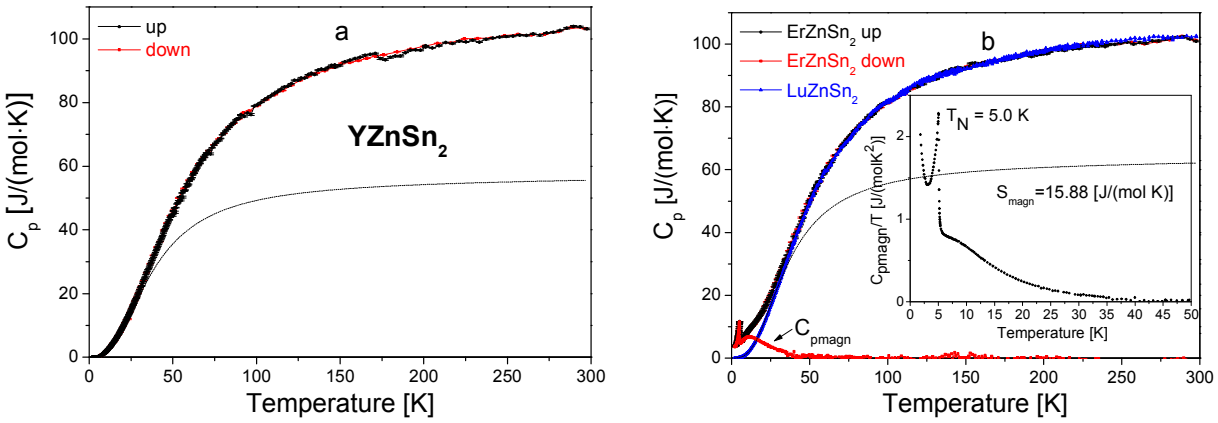

Fig. 2. Temperature dependencies of the specific heat (C_p) for the $YZnSn_2$ (a) and $ErZnSn_2$ together with superimposed $LuZnSn_2$ and their difference marked as the C_{pmagn} . (b). Inset in Fig. 2b shows the low temperature part of C_{pmagn}/T vs. T dependence for $ErZnSn_2$. The dashed lines are fits to $YZnSn_2$ and $LuZnSn_2$ data, respectively, with the standard Debye expression for θ_D values obtained at low temperatures (i.e. θ_D = (155.5±4.0) K and θ_D = (148.0±3.0) K for Y and Lu compounds, respectively, see the text below).

As it is seen from Fig. 2, the data collected with rising (up) and decreasing temperature (down) show no hysteresis. To separate the magnetic contribution, C_{pmagn}, from the total specific heat measured for $ErZnSn_2$, C_p, the following expression was used: $C_p = C_{lat} + C_{pmagn}$, where C_{lat} represents the lattice contribution to the specific heat, including the conduction electron $C_{el} = \gamma T$ and the phonon part C_{ph}. Since at higher temperatures (i.e. higher than ~50 K) $C_p(T)$ curves for Er and Lu compounds coincide almost exactly (see Fig. 2b), one can take $LuZnSn_2$ compound as a good reference material enabling the estimation of C_{lat} for $ErZnSn_2$ and other magnetic members of $RZnSn_2$ family. Hence, the subtraction of both curves gives $C_{pmagn}(T)$ contribution for Er compound and, in turn, integrating $C_{pmagn}(T)/T$ one can get the magnetic entropy contribution, S_{magn}, that reaches 15.88 J/(mol·K), being less than $R\ln 16 = 23.05$ J/(mol·K), which is expected for the ground state $J = 15/2$ multiplet of Er^{3+}.

It is worth to note that the simple formula for $C_{lat} = C_{el} + C_{ph} = \gamma T + C_{ph}$ with C_{ph} given by the very well known Debye expression [13] in the form

$$C_{lat} = \gamma T + 9R\left(\frac{T}{\theta_D}\right)^3 \int_0^{\frac{\theta_D}{T}} \frac{x^4 e^x}{(e^x - 1)^2} dx$$

does not fit properly C_p (T) curves obtained for Y and Lu compounds as well as that for Er (far above T_N) and this observation needs further analysis. It seems that the application of a more sophisticated analysis that includes a proper number of Einstein modes and anharmonic effects could improve remarkably the quality of such a fitting procedure.

Low temperature data for C_p/T obtained in the case of $YZnSn_2$ and $LuZnSn_2$ compounds are presented in Figs. 3a and 3b, respectively. They can be well fitted with a simple formula $C_p/T = \gamma + \beta T^2$ giving the electronic specific heat coefficients γ equal to (5.04±0.30) mJ/(mol·K^2) for $YZnSn_2$ and (5.75±0.20) mJ/(mol·K^2) for $LuZnSn_2$, respectively. These derived values of γ are typical for nonmagnetic rare-earth intermetallics, which is in full agreement with the previous magnetic measurements [1] where no long range magnetic ordering has been observed for both compounds.

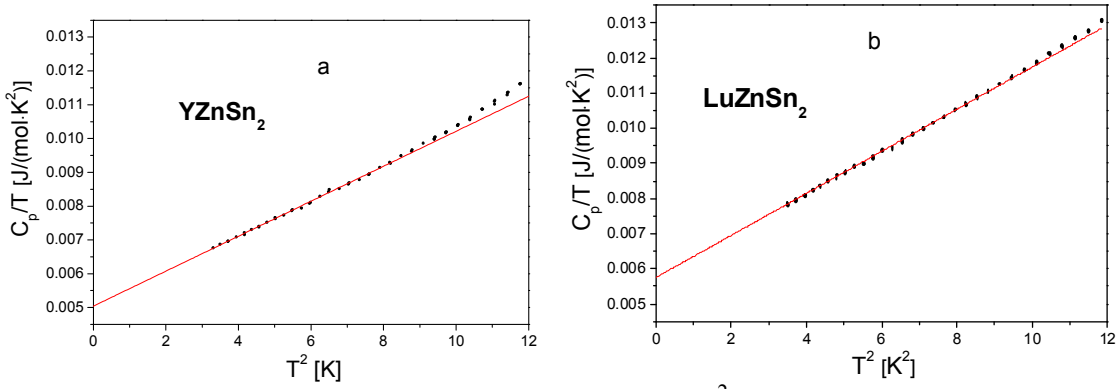

Fig. 3. Low temperature part of C_p/T dependencies on T^2 obtained for the $YZnSn_2$ (a) and $LuZnSn_2$ (b). The solid lines present the linear least-square fits used to derive the respective values of the specific heat coefficients γ and β for both compounds (see text).

The β coefficient is directly associated with C_{ph}, which at low temperatures ($T << \theta_D$) can be expressed as $C_{ph} = \beta T^3$ with $\beta = (12\pi^4/5)R/(\theta_D)^3$ [13] from where a Debye temperature θ_D value can be calculated. The β values obtained from the above discussed fits are $\beta = (5.17\pm0.40)\cdot10^{-4}$ J/(mol·K^4) for $YZnSn_2$ and $\beta = (5.99\pm0.04)\cdot10^{-4}$ J/(mol·K^4) for $LuZnSn_2$. In turn, the knowledge of β allows to estimate approximate Debye temperatures for both compounds and they are as θ_D = (155.5±4.0) K and θ_D = (148.0±3.0) K for Y and Lu compounds, respectively. The obtained values are very characteristic for R-T-X intermetallics. Additionally, one can also notice that estimated in such a way both γ values, as well as Debye temperatures θ_D, are quite comparable supporting the idea that the electronic properties and the phonon dynamics are very similar for $YZnSn_2$ and $LuZnSn_2$ compounds what, in fact, could be expected.

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