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Low temperature thermopower and magnetoresistance of Sc-rich $CeSc_{1-x}Ti_xGe$

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ABSTRACT

In $CeSc_{1-x}Ti_xGe$, Ti-alloying reduces the record-high antiferromagnetic (AFM) ordering temperature found in CeScGe at $T_N = 46$ K and induces ferromagnetism for $x \geq 0.5$. In this work we focus on the AFM side, i.e. Sc-rich samples, and study their thermopower $S(T)$ and magnetoresistance $\rho(H, T)$. The measured $S(T)$ is small in comparison with the thermopower of other Ce-systems and shows some features that are compatible with a weak hybridization between the $4f$ and band states. This is a further hint pointing to the local character of magnetism in this alloy. Magnetic fields up to 16 T have a minor effect on the electrical resistivity of stoichiometric CeScGe. On the other hand, for $x = 0.65$, we find that fields above 4 T suppress the hump in $\rho(T)$. Furthermore, the 4.2 K magnetoresistance displays a strong decrease in the same field range, also in coincidence with magnetization results from the literature. Our results indicate that $\rho(T, H)$ is a proper tool to assess the $H - T$ phase diagram of this system.

1. Introduction

CeScGe crystallizes in the La_2Sb-type tetragonal structure [1], with nearly two-dimensional Ce double layers intercalated by Sc and Ge along the $c-$axis. This compound stands out as having the highest antiferromagnetic (AFM) ordering temperature among Cerium-based magnetic systems, T_N=46 K [2–4]. As proposed in Ref. [5] and later verified by powder neutron diffraction experiments [6], at the Néel temperature the double layers order ferromagnetically (FM) and couple AFM along the $c-$axis. Between T_N and T_L=36 K [5], Ce magnetic moments lie in the basal plane [6]. When cooling below T_L, there is a canting of the moments towards the $c-$axis concomitant with a structural transition from tetragonal to triclinic of magnetostructural origin [6].

By introducing smaller Ti ($3d^2$) in the Sc-site ($3d^1$) the basal plane contracts, while the interlayer distance along the $c-$axis is practically preserved: these structural and electronic changes should strongly affect the magnetism. The magnetic phase diagram of the $CeSc_{1-x}Ti_xGe$ alloy was reported in Ref. [5]. Both $T_N(x)$ and $T_L(x)$ decrease at different rates, merging at a critical point $x_c \approx 0.35$ at $T_N \approx 20$ K. At $x \sim 0.45$ the ordering transition changes to ferromagnetic, dropping continuously down to T_C=7 K at $x = 0.75$, the limit of the La_2Sb-type structure. From this research it was concluded that in CeScGe the Ce-$4f$ orbital responsible for magnetism has a local character and that a number of factors, such as an optimized RKKY interaction and a low lying crystal field excited doublet at $\Delta_I/k_B \sim 35$ K $\sim T_N$, converge to produce the large ordering temperature.

Thermopower, $S(T)$, is a convenient tool to study hybridization and crystal field effects in Cerium compounds, while resistivity and magnetoresistance measurements, $\rho(T, H)$ can provide further information on the onset and stability of the magnetically ordered state and the nature of those phases. In this work, we present first results of a combined study of Sc-rich $CeSc_{1-x}Ti_xGe$ using these techniques.

2. Experimental details

Well-annealed $CeSc_{1-x}Ti_xGe$ polycrystalline samples were obtained by conventional synthesis and characterization techniques, as described in Ref. [5]. The samples for electrical resistivity and Seebeck coefficient measurements were cut using a low-speed diamond saw to typical sizes of $1 \times 1 \times 10$ mm^3. Both zero-field and in-field $\rho(T)$ measurements using a conventional four probe technique were performed with a LR700 ac resistance bridge. A zero-Lorentz force configuration $j||H$ was chosen for the magnetoresistance measurements in the $0 \leq \mu_0 H \leq 16$ T field-range. Fine-wire leads were spot-welded to obtain reliable low resistance contacts. Gold wire ($\phi = 50$ μm) was used for the resistivity, while

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AuFe 700 ppm (ϕ = 75 μm) and chromel (ϕ = 25 μm) were used for the thermopower measurements described below.

Thermopower at zero field was measured with a technique involving a heater and two thermocouples: chromel-sample and AuFe-sample; for further details see Ref. [7]. Additionally, the $S(T)$ of sample $x = 0.1$ was measured by means of a modulation technique involving two EG & G 5302 lock-in amplifiers with sinusoidal or square-wave excitations at a frequency of 30 mHz. This technique allowed us to perform measurements with lower noise levels and temperature variations well below the typical $\Delta T \sim 0.01$ T intended to explore eventual small anomalies in $S(T)$ close to the ordering transitions.

3. Results and discussion

In Fig. 1 we present the thermopower $S(T)$ of four different samples with Ti-concentration between $x = 0$ and 0.5. Our measurement on CeScGe confirms a previous result reported in Ref. [8] that found a sizable negative thermopower at high temperatures. Indeed, our data reaches $S \approx -11$ μV/K around 300 K, a value seldom observed in magnetic Ce-compounds in this temperature range. As Ti is introduced, the room temperature absolute thermopower is strongly reduced and changes sign for $x \sim 0.2$, reaching $S(300\ \text{K}) \approx 2$ μV/K for $x = 0.35$ and 0.5. This indicates a change from electron to hole-like carriers at room temperature with increasing x, probably dominated by changes in the diffusion contribution of band electrons. This contribution is expected to be relevant in view of the size of $S(T)$ in LaScGe reported in Ref. [8], also included for comparison in Fig. 1.

We now focus on the $T-$ dependence of the data for $T > 50$ K, i.e. above the Néel temperature of the stoichiometric compound. In all four samples we find a similar negative slope of $S(T)$ down to $T \sim 150$ K. In the case of CeScGe, $S(T)$ is negative and starts flattening below that temperature. In the case of $x = 0.1$, we find an initially negative thermopower that changes sign around 200 K and develops a maximum around $T^S_{max} \approx 80$ K. The $S(T)$ data for samples with $x = 0.35$ and 0.5 is positive and very similar in this $T-$ range, displaying the maximum at $T^S_{max} \sim 120$ K. In view of the small magnitude of $S(T)$ at the maximum, the shift in $T^S_{max}(x)$ and even its disappearance for $x = 0$ could be due to the changing contribution of band electrons mentioned in the previous paragraph.

One or two maxima are usually detected in the thermopower of intermetallic Cerium compounds, with typical values of the order of several tens of μV/K [9]. Calculations based on the single impurity Anderson model that take into account the crystal-field (CF) splitting of the 4f $J = 5/2$ ground-state (GS) multiplet and its coupling with the conduction band, are able to mimic different $S(T)$ dependences found experimentally [10]. In particular, we refer to figure 7 of Ref. [10] that displays $S(T)$ for different values of the hybridization strength $\Gamma < 2\Delta$, where $\Delta/k_B \sim 800$ K is the CF splitting between a Γ_7 doublet GS and an excited Γ_8 quartet (cubic) or two nearby doublets ($\Delta_1 \approx \Delta_2$, for non-cubic crystals).[1] It is found that for weak hybridization, $\Gamma \sim 60-70$ meV, $S(T)$ is relatively smaller (it is actually negative) and displays a maximum at $k_B T^S_{max} \sim 0.4\Delta$. Applying these results to the system at hand, one would also expect a weak hybridization $\Gamma \lesssim \Delta$ with a crystal field separation $\Delta_2 \sim 300$ K for $T^S_{max} \sim 120$ K.

Below 50 K, the almost flat $S(T)$ of CeScGe gives way to a steep increase ($|S(T)|$ decreases) that signals the transition at T_N. The spin-reorientation transition at T_L is almost undetectable, involving a minute change in dS/dT; notice the arrows that identify both ordering temperatures as extracted from specific heat measurements [5]. In the case of the $x = 0.1$ sample, a different behavior is observed since $T_N(0.1)$ is almost undetectable while a minimum appears close to $T_L(0.1)$. For $x = 0.35$ both transitions have almost merged, see Ref. [5], and manifest in the thermopower as a feature that has some resemblance to the hump observed in the electrical resistivity. For $x = 0.5$, our data do not allow to identify an anomaly in $S(T)$ at $T_C(0.5)$.

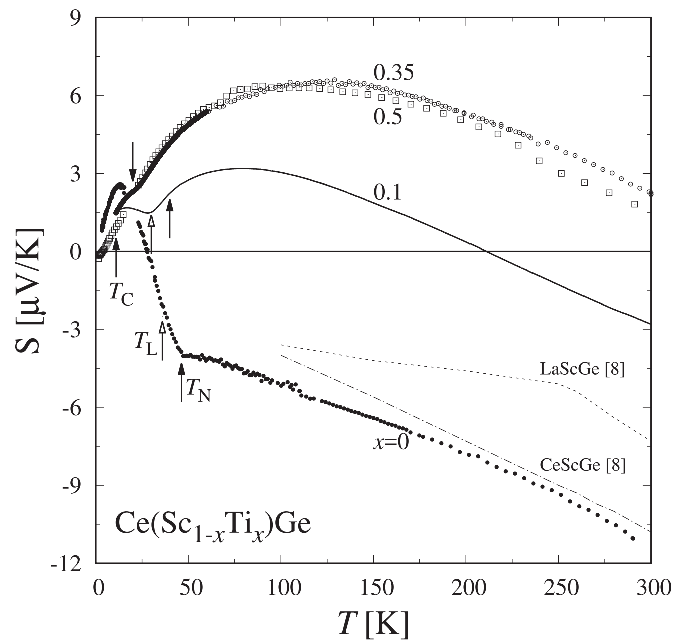

Fig. 1. Thermopower $S(T)$ of $CeSc_{1-x}Ti_xGe$ for $0 \le x \le 0.5$. Our data is compared with results for LaScGe and CeScGe from Ref. [8]. The origin of the break in the LaScGe data around 250 K is unknown. The arrows indicate the temperatures of the $T_N(x)$, $T_L(x)$ and $T_C(x)$ magnetic transitions, as extracted from specific heat measurements [5].

Now we turn to the electrical resistivity results under applied magnetic fields, measured in samples with $x = 0$ and 0.35. The inset of Fig. 2 depicts our $\rho(T)$ zero-field data for CeScGe. Our result is similar to that of a previous report [3], although it displays a larger residual resistivity ratio, $RRR \equiv \rho(300\ \text{K})/\rho(T \to 0) \approx 14$. The resistivity is roughly linear down to 50 K, displaying a clear anomaly at the Néel temperature $T_N \approx 46$ K, below which a stepper decrease is observed. The main panel of Fig. 2 allows one to analyze $\rho(T)$ at the transition in more detail: the curve tends to flatten out across T_N and becomes steeper below, showing a plateau of roughly 1 K around T_N. We describe this feature as a "hump", due to its similarity with anomalies reported in the literature for the resistivity of numerous systems displaying antiferromagnetic and spin-density wave (SDW) transitions.[2] For the sake of simplicity, in this case we identify the position of the hump by the point of the curve where $d\rho/dT$ is at a minimum. Our data shows that this feature remains roughly at the same temperature while it broadens with increasing field. Thus, in CeScGe the magnetic transition at T_N is almost unchanged under applied magnetic fields up to $\mu_0 H \sim 16$ T. Notice that the magnetoresistance changes sign from negative above T_N to positive, as it is usually the case for simple metals, for $T < 20$ K. In particular, the positive magnetoresistance dependence at 4.2 K is depicted in the inset of Fig. 3.

As reported in Ref. [5], the addition of Ti in $CeSc_{1-x}Ti_xGe$ leads initially to an increase of the size of the hump in $\rho(T)$, reaching a maximum at $x = 0.2$ and decreasing for $x > 0.2$. The hump is still

[1] This CF scheme is not directly applicable to the case of $CeSc_{1-x}Ti_xGe$, since in this alloy the first excited doublet is close to the GS-one while the second excited doublet is further away, i.e. resembling a quartet Γ_8 GS and an excited doublet, Calculations comparing the resistivities of both possible cubic-symmetry schemes, Γ_7–Γ_8 and Γ_8–Γ_7, are available in Ref. [13]. The relative contribution of a high temperature maximum in $\rho(T)$ is much smaller when Γ_8 is the ground state. This would mean that a further reduction in absolute value of the calculated $S(T)$ could be expected, providing a better agreement with our measurements.

[2] A clear hump-like anomaly for CeScGe is resolved in the excess resistivity once a phonon-like contribution is substracted to the $\rho(T)$ data, Something similar is observed, for example, in the electrical resistivity data of Chromium at high pressures displaying SDW magnetic ordering [11].

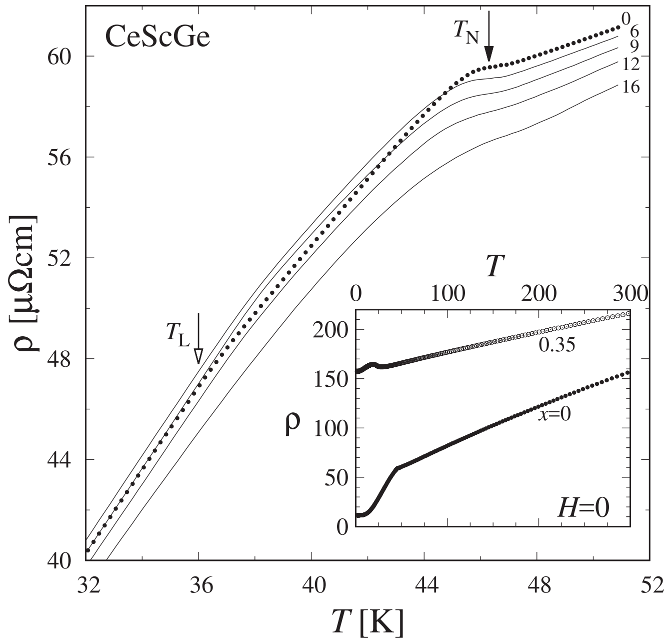

Fig. 2. Detail of the electrical resistivity $\rho(T)$ of CeScGe close to the ordering transitions with applied fields of $\mu_0 H$ = 0, 6, 9, 12 and 16 T (labeled at the top-right). The arrows signal T_N and T_L, as extracted from specific heat measurements [5]. Inset: zero-field $\rho(T)$ data for $x = 0$ and 0.35.

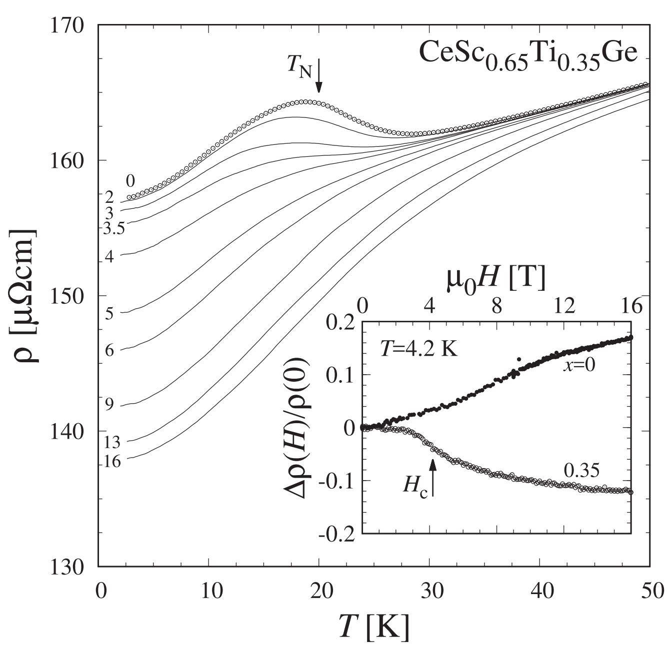

Fig. 3. Electrical resistivity $\rho(T)$ of CeSc $_{0.65}$ Ti $_{0.35}$ Ge below 50 K in zero and applied fields $\mu_o H$ = 2, 3, 3.5, 4, 5, 6, 9, 13 and 16 T (labeled at the center-left). The arrow signals T_N, as extracted from specific heat measurements [5]. Inset: relative magnetoresistance $\Delta\rho(H)/\rho(0) \equiv (\rho(H) - \rho(0))/\rho(0)$ at 4.2 K for samples $x = 0$ and 0.35. The arrow signals the critical field H_c, see the text.

clearly detected for $x = 0.35$, as it can be seen both in the inset of Fig. 2 and the main panel of Fig. 3. Again, an arrow indicates the position of T_N from Ref. [5], that in this case is close to the position of the maximum in $\rho(T)$. This T_N seems to underestimate the location of the magnetic transition as detected from the resistivity measurement, that should be closer to the onset of the hump, i.e. $T_N^\rho > T_N$. We again adopt a simple approach and follow the position of the largest (negative) slope in $d\rho/dT$, $\widetilde{T}_N$, located in between T_N and T_N^ρ. What we observe is that applied magnetic field progressively suppresses the hump until it is no longer detected for $\mu_0 H > 4$ T. For fields above 4 T, the resistivity displays a smooth change of convexity that shifts to higher temperatures with increasing field. Notice however, that $\widetilde{T}_N(H)$ is only weakly affected by H.

The 4.2 K magnetoresistance of the sample with $x = 0.35$ is negative, displaying roughly a 20 μΩ cm change between 0 and 16 T. The relative magnetoresistance $\Delta\rho(H)/\rho(0)$, inset of Fig. 3, is not large due to the large residual resistivity of this alloy. The maximum slope of $\Delta\rho(H)/\rho(0)$ is located at a critical field $\mu_0 H_c \approx 4.2$ T, that is consistent with the field applied to suppress the hump. Above this magnetic field one would expect to find a polarized state, with a high-magnetization state like the one detected above 4 T in magnetization measurements, see Ref. [5]. Notice that for $x = 0.35$ the ratio $\mu_0 H_c / T_N \approx 0.2$ lies among the lowest ratios reported for heavy fermion antiferromagnets [12] and that it is expected to decrease continuously as Ti-alloying approaches $x \sim 0.45$ (recall that for $x \geq 0.5$ a ferromagnetic ground state is found).

In magnetic systems like $CeSc_{1-x}Ti_xGe$, a hump in $\rho(T)$ usually relates to a gap opening at the magnetic ordering transition that affects a portion of the charge carriers: in this case it seems to be a *superzone gap* arising in a local moment system. The analysis presented above leads us to suggest that the occurrence of the resistivity hump provides a way to trace the antiferromagnetic phase along the $T - x - H$ phase diagram. The hump-like anomaly detected in $\rho(T)$ for $x = 0$ would then be related to an AFM state surviving even at the high-field range $\mu_0 H \sim 16$ T.

In view of our results, an open question is why a gap measured in $\rho(T)$ is not affecting $S(T)$ in a similar way. This question is perhaps more general, since many magnetic transitions show up in $\rho(T)$ but not in $S(T)$. Lacking a clear answer, one may speculate that this could be a consequence of a multiband scenario that should apply to the system at hand. Furthermore, a large degree of substitutional disorder as found in the $CeSc_{1-x}Ti_xGe$ alloys would also affect the measured thermopower $S(T)$: according to the Nordheim-Gorter rule applied to a magnetic system, one may consider magnetic, phononic and impurity/disorder contributions and write: $S(T) = (\rho_{mag}/\rho)S_{mag} + (\rho_{pho}/\rho)S_{pho} + (\rho_0/\rho)S_0$ [14]. In such alloys, $\rho(T)$ is dominated by the residual resistivity with $\rho_0 \gg \rho_{mag}(T)$, particularly at low temperatures. Then, the prefactor $\rho_{mag}/\rho \ll 1$ would result in a small contribution from $S_{mag}(T)$ to the total $S(T)$. Further work, including measurements on non-magnetic reference alloys, is underway in order to clarify this point.

4. Summary

Our results on $CeSc_{1-x}Ti_xGe$ show that in this system the thermopower $S(T, x)$ has a reduced absolute value in comparison with other Ce-based systems. This implies a minor contribution from the $4f^1$ state of Ce to $S(T)$, which seems to be a consequence of a weak coupling with conduction band states. A numerical estimation of the overall crystal-field splitting, $\Delta \sim 300$ K, serves as a means to assess the validity of this scenario. Additional valuable information could come from the measurement of some of the non-magnetic references, e.g. the equivalent La-compounds.

Magnetoresistance measurements show that magnetism in CeScGe is robust in fields up to 16 T, showing a hump-like anomaly in the resistivity in the whole field range. However, in the sample with $x = 0.35$ a relatively weak field around 4 T is enough to induce a metamagnetic transition despite its still large ordering temperature. Proper composition tuning could provide a sample with a very low critical field and large dM/dH.

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