From magnetic to Fermi Liquid behavior in CeCo$_{1-x}$Fe$_x$Si alloys

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Structural, magnetic and thermal measurements performed on CeCo$_{1-x}$Fe$_x$Si alloys are reported. Three regions can be recognized: i) Co-rich ($x \leq 0.20$) with a decreasing long range antiferromagnetic order which vanishes at finite temperature, ii) an intermediate region (0.20 < $x$ ≤ 0.30) showing a broad magnetic anomaly ($C_A$) in specific heat and iii) the non-magnetic region progressively changing from a non-Fermi-liquid type behavior towards a Fermi liquid one as Fe concentration increases. The $C_A$ anomaly emerges as an incipient contribution above $T_N$ already at $x = 0.10$, which indicates that this contribution is related to short range correlations likely of quasi-two dimensional type. Both, $T_N$ transition and $C_A$ anomaly are practically not affected by applied magnetic field up to $B \approx 10$ Tesla.

I. INTRODUCTION

Magnetic correlations play a basic role in systems accessing to phase transformations [1]. Besides canonical thermal fluctuations driving a 3-dimensional (3D) magnetic system into a long range magnetic order (LR-MO) ground state (GS), there are different types of fluctuations allowing to explore alternative minima for its free energy. For example, novel exotic phases may occur due to geometrical frustration as alternative GS [2]. Low dimensionality is another factor that enhances fluctuations due to geometrical constraints on the propagation of the order parameter.

Magnetic interactions in intermetallic compounds are mainly driven by the well know RKKY mechanism, which is essentially of 3D character. Although real low dimensionality is unlikely in intermetallic compounds, strongly anisotropic structures favor similar effects like in those systems resembling multilayer structures [3]. Among Ce equi-atomic ternaries, CeFeSi and CeScSi type structures provide the possibility to explore that alternative. The tetragonal CeFeSi-type structure builds up from two consecutive square planes (with W-type configuration) stacked up along ‘c’ direction with BaAl$_4$ blocks, following the Ce-Ce-Si-Fe$_2$-Si-Ce-Ce sequence.

In this work we report on structural, magnetic and thermal properties of CeCo$_{1-x}$Fe$_x$Si alloys investigated all along the concentration range. The respective stoichiometric limits are antiferromagnetic with localized $4f$ moments (CeCoSi, $T_N = 8.8$ K [4]) and non-magnetic showing intermediate valent (Ce-FeSi) behavior [5]. Thus, this system allows to run through a critical region where magnetic order vanishes.

II. EXPERIMENTAL RESULTS

A. Structural properties

The relevant interatomic distances in the CeFeSi-type structure are the following: $d_{T-X}, d_{R-T}$ and

FIG. 1. (a) $c/a$ lattice parameters ratio and (b) unit cell volume variation as a function of Fe content in CeCo$_{1-x}$Fe$_x$Si (left axis). Respective reference parameters form LaCo$_{1-x}$Fe$_x$Si are included (green) using the right axis. Dash-dot and dash curves are guide for the eye.
\[ d_{R-X}, \text{ being R the rare earth (Ce in this case), T the transition metal (Co/Fe) and X the semimetal (Si). The crystal chemistry study performed on the isotypic compound LaFeSi} \text{ indicates a reduction of the mentioned distances respect to the corresponding values of respective pure elements: } \Delta_T - \Delta_{R-Si} = [d_T - (d_T + d_{Si-Si})] / [d_T + d_{Si-Si}] * 100 = -0.084\%, \Delta_{R-Si} = -0.027\% \text{ and } \Delta_{R-X} = -0.024\%, \text{ whereas the other distances: } \Delta_T - \Delta_{R-X} \text{ and } \Delta_{R-R} \text{ increase. The large contraction observed on } \Delta_T - \Delta_{R-Si} \text{ is related to the strong electronic hybridization between those atoms. This explains the non-magnetic behavior of Fe (or Co) atoms as a consequence of a large band width.}

In the system under study, two regions can be clearly distinguished in the concentration dependence of the lattice parameters, see Fig. 1. On the Co-rich side there are minor variations up to about 20\% of Fe doping. Beyond that concentration, a clear modification occurs in the variation of both tetragonal axis: \( a(x) \) increasing about 1\% whilst \( c(x) \) decreases about 5\% once it reaches the CeFeSi stoichiometric limit. Fig. 1(a) shows a significant reduction of the \( c/a \) ratio (about 3.5\%), coincident with a decrease of the unit cell volume (about 1.3\%), shown in Fig. 1(b). This structural variation tends to reduce Ce-Ce spacing \( d_{Ce-Ce} \) between neighbors placed on the apex and on the square-base pyramids formed by each Ce double layer.

The volume variation above \( x \approx 0.20 \) (see Fig. 1) largely exceeds the equivalent variation for neighboring lanthanides (i.e. La and Pr) as a sign of the Ce-4f orbitals instability with Fe content increase. As a reference, the respective values of three La(Co,Fe)Si samples are included in Fig. 1(a) and (b) on the right axis. The increase of volume between LaTSi (\( T = \text{Co and Fe} \)) compounds contrasts with the strong decrease in CeCo\(_{1-x}\)Fe\(_x\)Si alloys, indicating the collapse of Ce atomic volume for \( x \geq 0.20 \). In fact, the CeCoSi unit cell volume is \( \approx 1\% \) below the interpolation between LaCoSi and PrCoSi, whereas CeFeSi is \( \approx 4\% \) below the equivalent La to Pr interpolation.

**B. Magnetic properties**

The inverse of the high temperature magnetic susceptibility is shown in Fig. 2(a), from which a Curie constant close to the \( J = 5/2 \) Hund’s rule GS value is extracted from \( T > 50 \text{K} \) for the \( x \leq 0.10 \) alloys. Beyond that Fe concentration, the Curie constant starts to decrease in coincidence with the increase of the paramagnetic temperature \( \theta_P(x) \) as presented in the inset of Fig. 2(a). Higher Fe concentration samples show low temperature ferromagnetic contributions that become important as the main magnetization decreases. Whether this is an intrinsic effect or due to a foreign contribution is under investigation.

The relatively high value of \( \theta_P \) at low Fe content is likely due to a combination of Kondo effect acting on respective CEF levels and RKKY exchange. The up turn of \( \theta_P(x) \) beyond \( x = 0.20 \) is due to a strong increase of Kondo screening related to the significant volume reduction. The corresponding Kondo temperature \( (T_K) \) is evaluated following Krishna-Murthy criterion: \( T_K = -\theta_P/2 \).

Details of the low temperature magnetic behavior are presented Fig. 2(b), showing the decrease of the maximum of \( M(T) \) at the anti-ferromagnetic ordering from \( T_N = 9 \text{K} \) at \( x = 0 \) down to \( \approx 2 \text{K} \) at \( x = 0.30 \). The later is hardly seen in Fig. 2(b), because it contains curves performed with an applied magnetic field of \( B = 1 \text{T} \), albeit the maximum is clearly observed in lower applied field e.g. \( B = 0.03 \text{T} \) (not shown).
The magnetic contribution to the specific heat \( C_m \) is obtained after subtracting the phonon contribution extracted from the isotopic La compound. The results of all studied samples are collected in Fig. 3. Three distinct behaviors are observed in different concentration ranges: (a) on the Co-rich side with a rapidly decrease of the \( C_m(T_N) \) jump \( \Delta C_m(T_N) \) within the 0 ≤ \( x \) ≤ 0.20 concentration range, (b) a broad anomaly \( C_A \) that becomes dominant between \( x = 0.23 \) and 0.32, and (c) a non-magnetic region for \( x \geq 0.35 \).

C. Specific heat

The magnetic contribution to the specific heat \( C_m \) is obtained after subtracting the phonon contribution extracted from the isotopic La compound. The results of all studied samples are collected in Fig. 3. Three distinct behaviors are observed in different concentration ranges: (a) on the Co-rich side with a rapidly decrease of the \( C_m(T_N) \) jump \( \Delta C_m(T_N) \) within the 0 ≤ \( x \) ≤ 0.20 concentration range, (b) a broad anomaly \( C_A \) that becomes dominant between \( x = 0.23 \) and 0.32, and (c) a non-magnetic region for \( x \geq 0.35 \). Although these three regions are clearly distinguishable, the onset of the \( C_A(T) \) anomaly is already detected at lower Fe concentration right above the \( T_N(x) \) transition. Notably, this incipient anomaly starts to develop at \( T \approx 10 \approx T_N(x = 0) \) K. This fact indicates that the anomaly builds up from the same degrees of freedom but governed by short range magnetic interactions.

As the \( \Delta C_m(T_N)/T \) jump weakens and the \( C_A \) anomaly becomes dominant, also an underlying Kondo type contribution arises. This contribution is related to the formation of heavy fermion (HF) quasi-particles. The low temperature value of this HF contribution increases continuously with \( x \) as indicated by the \( C_m/T \bigg|_{T \rightarrow 0} \) \( x \) values at 0.5 K. At \( x = 0.35 \), a non-Fermi-liquid (NFL) type dependence: \( C_m/T \propto -\log(T) \) is clearly seen, although it tends to flatten at low temperature. For \( x > 0.5 \) a progressive transformation into a Fermi-liquid regime occurs as the Ce-lattice enters into a valence instability regime concomitant with the Ce-volume reduction.

The temperature of the specific heat jump at \( T_N \) does not coincide with the maximum of \( M(T) \) but with the maximum of its \( \partial M/\partial T \) derivative. This is a typical sign of low dimensionality or strong anisotropy character of magnetic interactions [1].

III. DISCUSSION

A. Phase diagram

The concentration dependence of the relevant parameters is resumed in a schematic phase diagram in Fig. 4. It includes the \( T_N(x) \) decrease together with the respective specific heat jumps \( \Delta C_m(T_N)/T \) reduction that vanishes at \( x = 0.23 \). The decreasing height of \( \Delta C_m/T \) at \( T = T_N(x) \) is qualitatively represented in the figure as a segment at-
attached to each point. The $C_A(T)$ anomaly is represented by the characteristic temperature $T_N(x)$ defined in Fig. 5(b) as the temperature of the maximum negative $\partial C_A/\partial T$ slope above $T_N(x)$. The HF component is represented by the $C_m/T$ values at $T = 0.5K$, which increases in the region $0 < x < 0.35$ where degrees of freedom are progressively transferred from the ordered phase into the heavy quasiparticles. Beyond that concentration, $C_m/T$ decreases with $x$, since $C_m/T \propto 1/T_K$ the Kondo temperature increases as expected for a non-ordered Kondo lattice.

### B. On the nature of the specific heat anomaly

The origin and nature of the $C_A(T)$ anomaly deserves a more detailed analysis. As mentioned before, it emerges like a $T > T_N(x)$ tail as soon as $T_N(x)$ starts to decrease and is fully developed once the LR-MO phase is suppressed before the Kondo effects starts to dominate the low temperature behavior. We notice that the temperature dependence $C_m \propto T^2$, observed below $T_N(x)$ between $x = 0$ and $x = 0.35$, remains unchanged even once the $\Delta C_m/T_N$ vanishes at $x = 0.23$. These features indicate that the $C_A(T)$ anomaly builds up from the magnetic degrees of freedom which at lower Fe concentration are involved in the LR-MO phase formation. This anomaly very likely corresponds to short range magnetic correlations of quasi two-dimensional (2D) type within the double Ce layer. The increasing Kondo interaction and the atomic disorder in the Co/Fe-Si layer in between very likely results in a weakening of the magnetic interactions along 'c' direction and then to a transition from a 3D to a quasi 2D- system.

In order to gain insight into the characteristics of this anomaly, we have performed thermal expansion $(\alpha)$ measurements at zero and under strong magnetic field $(B = 10T)$ on sample $x = 0.15$. At that Fe concentration both, the incipient $C_A$ anomaly and the $T_N$ transition are competing, see Fig. 5(a). For comparison, zero field specific heat and electrical resistance $(R)$ are included in Fig. 5(b). The temperature dependence of these three properties coincide in showing the onset of the anomaly contribution at $T \approx 12.5K$, being $\alpha(T)$ the more sensitive to the appearance of those magnetic correlations. Incipient coherence effects are observed in the $R(T)$ dependence starting at $T \approx 13K$. This temperature coincides with the onset of the $C_m(T)$ upturn approaching the magnetic transition.

Notably, applied magnetic field of $B = 4T$ (not shown) produces no relevant effects neither on the anomaly nor on the $T_N$ transition. A $B = 10T$ field weakens the anomaly without affecting the $T_N$ transition (see Fig. 5(a)) like in stoichiometric CeCoSi [9]. Furthermore, a slight shift of the transition to lower temperature (to $T_N \approx 5K$) is only observed by applying a field $B = 16T$. Preliminary $M(B)$ measurements up to $B = 5T$ show a very weak upturn from a linear dependence for $B \geq 4T$, with coincident values obtained at $T = 1.8, 3$ and $5K$.

### IV. SUMMARY

Although the magnetic order of this system vanishes as expected, the phase boundary of the long range magnetic order does not extrapolate to $T = 0$. Instead we observe a progressive substitution of the LR-MO by short range interactions. A broad anomaly arises between the $T_N(x = 0)$ temperature and the actual decreasing $\Delta C_m(T_N(x))$ jump of each alloy. These features suggest that the involved magnetic degrees of freedom are transferred from one component to the other. Notably, the magnetic interactions in this system are very robust against external magnetic field application because both, $C_A$ anomaly and the $\Delta C(T_N)$ jump, require $B \geq 10T$ and $B \geq 14T$ to be suppressed or shifted respec-
Beyond the $C_A$ phase formation, the complex phase diagram shows how the magnetic degrees of freedom from the Co-rich side are transferred to a heavy quasiparticles component exhibiting a NFL type behavior. Once the full NFL regime is reached around $x \approx 0.35$, $T_K$ increases rapidly towards the Fe-rich side. The large value of $\theta_P$ and the entropy gain with temperature indicates that the first excited CEF level is also affected by the Kondo effect and partially contributes to the low temperature properties. Further studies are in progress to better elucidate the exotic characteristics of the $C_A$ anomaly and the significant magnetic hardness of these alloys.

This investigation confirms that Ce-equiatomic ternary compounds with strongly anisotropic structures allows to access to novel behaviors where enhanced fluctuations can play an important role.

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