An unusual interplay among disorder, Kondo-effect and spin-glass behavior in the Kondo lattices, Ce$_2$Au$_{1-x}$Co$_x$Si$_3$

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We report the results of magnetic measurements for the solid solution Ce$_2$Au$_{1-x}$Co$_x$Si$_3$. The results reveal that this solid solution is characterized by a magnetic phase diagram (plot of magnetic transition temperature versus $x$) unusual for Kondo lattices. In particular, the spin-glass freezing induced by disorder is observed only for the compositions at the weak coupling limit; as one approaches the quantum critical point by a gradual replacement of Au by Co, this disorder effect is surprisingly suppressed in favor of long range antiferro-magnetic ordering in contrast to expectations. This unusual interplay between disorder, spin-glass freezing and the Kondo-effect calls for further refinement of theories on competition between magnetism and the Kondo effect.

The study of the consequences of the competition between the Kondo effect and magnetic ordering in rare-earth and actinide systems continues to be an active topic of research. While the observation of long range magnetic ordering in some Kondo lattices itself is a subject of great theoretical interest considering that the Kondo effect should quench magnetism, one also observes disorder-induced spin-glass anomalies in the vicinity of quantum critical point (QCP) in some U and Ce systems (see, for instance, Refs. 1 and 2). This made this topic of research more fascinating and new theoretical ideas have been initiated in the recent literature under the assumption that such disorder effects are operative only at QCP. In this Letter, we bring out a counter-example, viz., the recently discovered solid solution, Ce$_2$Au$_{1-x}$Co$_x$Si$_3$, in which spin-glass behavior in fact is observed only when one approaches the weak coupling limit, that is, as one moves towards larger unit-cell volume. In otherwords, this glassy behavior surprisingly gets suppressed with increasing chemically-induced disorder as one approaches QCP, as though increasing Kondo interaction strength plays an unusual role of favoring long-range magnetic order at the expense of spin-glass behavior. This finding adds a new dimension to this direction of research, demanding further refinement of the theories on this subject.

These alloys, crystallizing in a AlB$_2$-derived hexagonal structure, have been found to exhibit many interesting magnetic characteristics. While the parent Au compound orders magnetically below about 3 K, Ce$_2$CoSi$_3$ is a non-magnetic Kondo lattice. As Au is progressively replaced by Co, the magnetic ordering temperature ($T_o$) goes through a maximum (to about 8 K) as a function of $x$. This observation indicated that this compound lies at the left hand side of the Doniach’s magnetic phase diagram. This alloy series is one of the few solid solutions spanning a wide range of Doniach’s magnetic phase diagram, thus serving an ideal series to test a theory for a large variation in the 4f exchange interaction strength. It is also to be noted that, for some intermediate compositions before the maximum, two magnetic transitions were observed with the previous data revealing interesting changes in magnetic structure both as a function of $x$ and $T$. This prompted us to investigate exact nature of these transitions in all these alloys to unravel the mysteries behind the competition between the Kondo effect and magnetism. We have therefore performed ac susceptibility ($\chi_{ac}$) measurements on many compositions of this alloy series at low temperatures. In addition, in order to augment the line of arguments of these alloys, we carried out low temperature isothermal magnetization (M) (in addition to that reported in Ref. 7) and low temperature heat-capacity (C(T)) of Ce$_2$Au$_{0.2}$Co$_{0.8}$Si$_3$. The knowledge thus gained viewed together with the findings reported in Ref. 7 enables us to construct a magnetic phase diagram.

The samples employed were synthesized as discussed in Ref. 7. The x ray diffraction patterns reveal that all the samples are single phases, though there could be a small amount of an impurity phase for $x=0.0$ if interpreted within AlB$_2$ structure. The $x=0.0$ sample is a single phase, the pattern is analysed in an orthohombic structure. For many alloys ($x=0.0, 0.1, 0.2, 0.3, 0.4, 0.6$ and $0.8$), $\chi_{ac}$ (1.8-15 K) was probed employing a commercial magnetometer at various frequencies ($1, 10, 100, 1000$ Hz). Isothermal dc M data were also collected below 12 K for some compositions at the Au rich end with the same magnetometers. We have also taken C
data down to 1.2 K to resolve the question whether the composition $x=0.8$ close to the QCP is a spin-glass.

In Fig. 1, we show $\chi_{ac}$ data, both for the real ($\chi'$) and the imaginary ($\chi''$) components, as a function of (logarithmic) $T$ below 12 K for $x=0.0$. There is a peak at about 3 K due to the onset of magnetic ordering consistent with the observation in the $C$ and $dc$ $\chi$ data. There is an additional peak at about 2.2 K (which could not be resolved in earlier studies due to non-accessibility of this $T$ range), establishing the existence of another magnetic transition. In fact two transitions could in principle be expected from two crystallographically inequivalent Ce sites for an ordered arrangement of Au and Si ions, for which there is an evidence from the doubling of a parameter of the unit-cell. Therefore, at present, we cannot resolve whether the double transition arises from these two sites or whether the same Ce ions undergo spin-reorientation as $T$ is lowered from 3 to 2.2 K. Our main conclusions are however not affected by actual reasoning about this T; the absence of spin-glass freezing for this composition (which is close to 7K-peak in the $C$ data in terms of Schottky anomalies. It may be recalled that, the isothermal M behavior at 5 K for $x=0.0$ does not exhibit such an effect, thereby ruling out antiferromagnetic state for this end member.

Spin glass features are seen for $x=0.3$ with a transition close to 5.3 K (with another feature at 2.7 K). It appears that the 7K-transition seen for $x=0.2$ has moved down to a lower temperature (close to 6 K) and now it appears as a tail above the peak in the $\chi'$ data. For $x=0.4$, however, there is only one magnetic transition at 5 K which nicely agrees with $C(T)$ and $dc$ $\chi$ data with a frequency dependence of the curve below the peak, classifying this composition also as a spin-glass. Interestingly, for $x=0.6$, not only the peak temperature (4.5 K) but also the values are frequency independent throughout the T range of measurement, as if this alloy cannot be classified as a spin-glass; in support of this, the $\chi''$ anomaly at the magnetic transition is negligible. Therefore, ZFC-FC $dc$ $\chi$ bifurcation reported earlier for this composition does not arise from spin glass freezing and it should be noted that such features have been observed in the past even in some long range magnetically ordered systems.

In short, judged by the frequency dependence of $\chi''$ below the peak as well as by distinct $\chi''$ features, we conclude that all the compositions below $x=0.6$ are spin-glasses at very low temperatures (typically below 4.5 K). However, long range magnetic ordering sets in at slightly higher temperatures for $x=0.1-0.3$.

We now turn to the magnetism of the Co-rich end. In order to probe this aspect, the $C$ measurements were performed down to 1.2 K for the composition $x=0.8$ and the results are shown in Fig. 2b. It is distinctly clear that there is a prominent peak at 2 K. In spin-glass systems, the corresponding feature in $C$ is broadened significantly and the observation of a well-defined peak therefore rules out spin-glass freezing for this composition (which is close to QCP, given that the end Co member is non-magnetic). The $\chi'$ data (Fig. 1) tends to show a flattening below 2 K (without any frequency dependence of absolute values) as though there is an onset of magnetic order very close to this T; the absence of $\chi''$ feature at 2 K also rules out
spin glass freezing for this composition.

We would like to mention that we have also measured MR ($=\frac{\rho(H)-\rho(0)}{\rho(0)}$) as a function of H down to 0.6 K primarily to support our conclusions for the compositions close to QCP ($x=0.6$ and 0.8). The MR of these alloys is found to be positive (typically close to 2%) even for reasonably large values of H (say till 40 to 60 kOe) well below their respective $T_o$, characterizing that these alloys are antiferromagnets without magnetic Brillouin-zone gap effects at temperatures as low as 0.6 K. If the low temperature state is a spin-glass, the sign of MR should be negative even in the low field range. We also observed a sign reversal at higher fields establishing the field-induced spin-flipping in these alloys. Above the respective ordering temperatures, MR is negative in the entire field range typical of paramagnets.

By consistently interpreting the features observed in all these data as well as dc $\chi$ and C features reported in Ref. 7, we have sketched a magnetic phase diagram (see Fig. 3) for the present solid solution. For this purpose, the onset of spin-glass freezing marked in Fig. 3 is inferred from the temperature at which $\chi'$ exhibits a sharp upturn, while the $T$ in the vicinity of which long range magnetic ordering sets in is inferred from the shoulder/peak temperatures in the $\chi'$ plots (Fig. 1). The additional spin-glass transition (around 2.5 K) seen in the ac $\chi$ data for the compositions $x=0.0$ to 0.3 is not marked in the figure separately for the sake of simplicity of the figure, particularly noting that these phases are also anyway spin-glasses. This transition must be intrinsic to the samples considering that the materials are essentially single phase and future investigations may focus on the exact origin of this phase. It may also be added that the absolute values of $T_o$ determined from different techniques slightly (to the extent of 0.5 K) vary, which is attributed to some degree of ambiguity in locating the actual transition point from different experimental techniques. Therefore, the values plotted are representative of the transition regions. In spite of these deficiencies, this pictorial representation serves as an useful guide to bring out the main points. To demonstrate the novelty of the magnetic phase diagram of this series, we compare our findings with that for a well-studied system, CeCu$_{1-x}$Ni$_x$ (compare with Fig. 3 in Ref. 2): (1) The magnetic phase diagram is reversed for both these two series of alloys, CeCu$_{1-x}$Ni$_x$ and the present one. (2) The ones that exhibit spin glass behavior in our solid solution fall in the low coupling regime (that is, close to or below the maximum of the Doniach’s magnetic phase diagram as inferred from the $x$ dependence of $T_o$), whereas the compositions close to QCP are not spin glasses. This observation is in sharp contrast to expectations based on previous knowledge in the field. (3) In some of the alloys with more than one magnetic transition, that is, in the range $x=0.1$ to 0.3, long range magnetic ordering precedes spin glass freezing as $T$ is lowered, in sharp contrast to the reverse behavior observed in the Ce-Cu-Ni series. To our knowledge, this kind of magnetic phase diagram has not been reported for any Kondo alloy in the past.

We like to add that, in the neutron diffraction data at 2 K for all compositions classified here as spin glasses, no additional sharp lines appear when compared with the data at 10 K. However, for $x=0.6$, distinct evidence for long range magnetic ordering is found in the neutron data. These neutron data thus endorse the main findings (summarised below) in this article.

To conclude, we have identified a Ce based solid solution in which increasing chemical disorder surprisingly suppresses spin glass behavior in favor of long range magnetic order as one moves towards Kondo-dominated state. It is intriguing to note that the disorder-induced spin-glass behavior is realised only at the weak coupling limit, but not close to QCP, in contrast to the hitherto observed, predicted or assumed behavior. Absence of this disorder effect at QCP is surprising, particularly considering that a stoichiometric end of the solid solution is by itself a spin-glass. It is therefore a real theoretical challenge to understand this unusual interplay among the disorder, spin-glass ordering and the Kondo effect.

One of us (EVS) would like thank C. Laubschat for a visit to Dresden under SFB463, during which this collaboration with Augsburg group was initiated. He also thanks Sarojni Damodaran Foundation for supporting the visit of Subham Majumdar to TU Vienna. Research in Vienna is supported by the Austrian FWF, project P 12899. We thank A. Szytula for bringing us to our attention the results of his neutron diffraction measurements before publication. We thank Kartik Iyer for his help in sample characterization and magnetization measurements.

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FIG. 1. Real (χ′) and imaginary (χ″) part of ac susceptibility as a function of temperature (logarithmic scale) below 12 K for the alloys, Ce$_2$Au$_{1-x}$Co$_x$Si$_3$, at various frequencies. Since, for x = 0.8, the data at various frequencies overlap, and hence we show the data only at one frequency (1 Hz).

FIG. 2. (a) Isothermal magnetization behavior of Ce$_2$Au$_{0.8}$Co$_{0.2}$Si$_3$ at selected temperatures; (b) Heat capacity as a function of temperature below 5 K for the alloy, Ce$_2$Au$_{0.8}$Co$_{0.2}$Si$_3$.

FIG. 3. Schematic representation of the magnetic phase diagram of the alloy series, Ce$_2$Au$_{1-x}$Co$_x$Si$_3$. $T_o$ represents magnetic transition temperature. The continuous lines through the data points serve as a guide to the eyes.
\[ M (\mu_B/\text{formula unit}) \]

\[ H (\text{kOe}) \]

\[ T (\text{K}) \]

\[ \text{Ce}_2\text{Au}_{0.9}\text{Co}_{0.1}\text{Si}_3 \]

\[ \text{Ce}_2\text{Au}_{0.2}\text{Co}_{0.8}\text{Si}_3 \]
The diagram shows the phase transition behavior of \( \text{Ce}_2\text{Au}_{1-x}\text{Co}_x\text{Si}_3 \) as a function of the composition \( x \). The phase transitions are indicated as follows:

- **Spin glass**
- **Antiferro**
- **Paramagnetic**
- **Antiferro**
- **Non magnetic Kondo lattice**

The horizontal axis represents the composition \( x \), ranging from 0.0 to 1.0, and the vertical axis represents the temperature \( T_0 \) in Kelvin, ranging from 0.0 to 8.0.