An unusual interplay among disorder, Kondo-effect and spin-glass behavior in the Kondo lattices, $Ce_2Au_{1-x}Co_xSi_3$

S. Majumdar[a], E.V. Sampathkumaran[a,*,1], St. Berger[b], M. Della Mea[b], H. Michor[b], E. Bauer[b], M. Brando[c], J. Hemberger[c], A. Loidl[c]

[a]*Tata Institute of Fundamental Research, Homi Bhabha Road, Colaba, Mumbai 400005, India*
[b]*Institut f.Experimentalphysik, Vienna University of Technology, A-1040 Wien, Austria*
[c]*Experimentalphysik V, Elektronische Korrelationen und Magnetismus, Institut für Physik, Universität Augsburg, D-86135 Augsburg, Germany*

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. [1,2]). 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 [3–5]. In this Letter, we bring out a counter-example, viz., the recently discovered [6,7] solid solution, $Ce_2Au_{1-x}Co_xSi_3$, 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 other words, 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 [7]. While the parent Au compound orders magnetically below about 3 K, Ce_2CoSi_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 [8]. This alloy series is one of the few solid solutions spanning a wide range of Doniach's magnetic phase diagram [8] 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

* Corresponding author. Tel.: +91-22-215-2971; fax: +91-22-215-2110.
E-mail address: sampath@tifr.res.in (E.V. Sampathkumaran).
[1] Honorary Faculty Member, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore-560064, India.

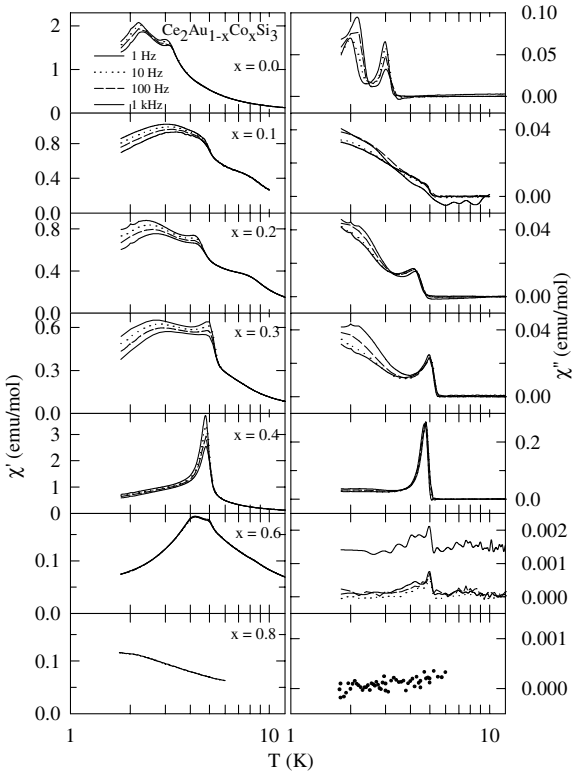

Fig. 1. Real (χ') and imaginary (χ'') part of ac susceptibility as a function of temperature (logarithmic scale) below 12 K for the alloys, $Ce_2Au_{1-x}Co_xSi_3$, at various frequencies. Since, for $x = 0.8$, the data at various frequencies overlap, and hence we show the data only at one frequency (1 Hz).

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 (χ_{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 $Ce_2Au_{0.2}Co_{0.8}Si_3$. 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, if the pattern is analyzed in an orthorhombic structure [7]. For many alloys ($x = 0.0$, 0.1, 0.2, 0.3, 0.4, 0.6, and 0.8), χ_{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 [7] whether the composition $x = 0.8$ close to the QCP is a spin-glass.

In Fig. 1, we show χ_{ac} data, both for the real χ' and the imaginary (χ'') 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 χ data [7]. There is an additional peak at about 2.2 K (which could not be resolved in earlier studies [6,7] due to non-accessibility of this T range), establishing the existence of another magnetic transition. In fact two transitions could in principle be expected [9] 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 [7]. 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 of these two transitions.

We now address the question whether the disordered alloys are spin-glasses and if so whether this changes with composition. For this purpose, we show in Fig. 1 the frequency dependence of χ_{ac} for several compositions ordering magnetically in the covered temperature range. It is a well known fact that the peak of χ_{ac} should not exhibit a frequency dependence for long range ordering at the transition temperature [10], but spin glasses, however, are characterized by a peak shift of the order of a few percent. This essentially means a shift of the peak by about 0.1 K in our alloys for a change of frequency from 1 Hz to 1 kHz, which can easily be missed if the peak is broad as it appears to be the case in the present series. However, we can draw an inference on the frequency dependence if the left part of the curve moves to a higher temperature with increasing frequency. Also, in spin glasses, χ'' shows a sharp and prominent anomaly near the transition [10]. If one looks for these two features, it follows that both the transitions for $x = 0.0$ interestingly could be due to spin-glass freezing. It is therefore clear that the broad $C(T)$ anomaly spreading over a wide temperature range [7] is associated with such a disordered magnetism.

With respect to the $x = 0.1$ and 0.2 compositions, magnetic transitions are observed in the vicinity of 7–8 K as well as close to 4.5 K, manifesting as a broad shoulder and a peak (or a sharp upturn) in χ', respectively; the 4.5 K-transition is of a spin-glass-type within the scope of the criteria stated above, but the 8 K-transition is not. This interpretation is consistent with the ZFC-FC dc χ behavior reported earlier [7]. Incidentally, there is also a prominent peak in $C(T)$ (see fig. 3 of Ref. [7]) around 7 K confirming the existence of another magnetic transition around this temperature. Correspondingly, inverse dc $\chi(T)$ also exhibits

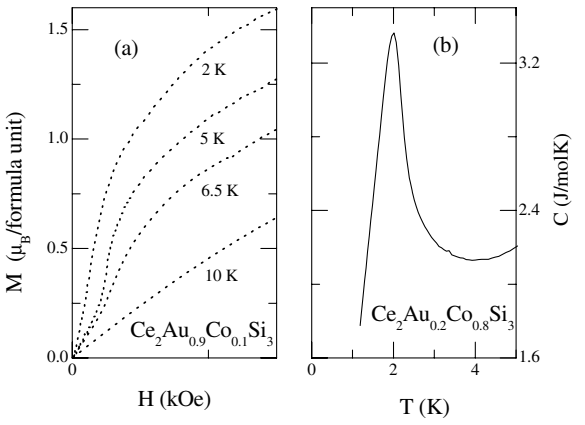

Fig. 2. (a) Isothermal magnetization behavior of $Ce_2Au_{0.9}Co_{0.1}Si_3$ at selected temperatures; (b) Heat capacity as a function of temperature below 5 K for the alloy, $Ce_2Au_{0.2}Co_{0.8}Si_3$.

a flattening below this temperature (see fig. 4 inset in Ref. [7]). The fact that the 7 K-transition arises from magnetic ordering only is established further from the isothermal M behavior discussed (in figs. 6 and 7) in Ref. [7]. We have taken additional M data at various temperatures at the Au rich end to strengthen our conclusions. The behavior of M for $x = 0.1$ below 15 K is shown in Fig. 2a to highlight the following point: while the plot is linear at 10 K typical of paramagnets, there is a sharp upturn of M beyond 2.5 kOe at 5 K. This feature becomes broader as one increases temperature, say, to 6.5 K. However, such a feature is absent at 2 K. The behavior is the same for $x = 0.2$. These observations suggest that there is a metamagnetic transition in a narrow temperature interval above 4.5 K. This establishes that the zero-field magnetic ordering in this narrow temperature range is of an antiferromagnetic type. We may add that the observation of such spin-reorientation effects in M data is not characteristic of Schottky anomaly, but only of antiferromagnetism, thereby conclusively ruling out any

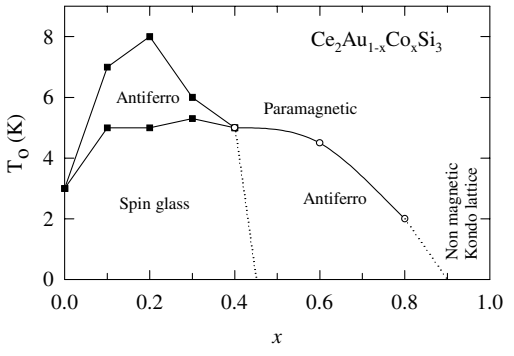

Fig. 3. Schematic representation of the magnetic phase diagram of the alloy series, $Ce_2Au_{1-x}Co_xSi_3$. T_o represents magnetic transition temperature. The continuous lines through the data points serve as a guide to the eyes.

explanation of the 7 K-peak in the C data in terms of Schottky anomalies. It may be recalled [7] 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 7 K-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 χ' data. For $x = 0.4$, however, there is only one magnetic transition at 5 K which nicely agrees with $C(T)$ and dc χ data [7], 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 χ'' anomaly at the magnetic transition is negligible. Therefore, ZFC-FC dc χ bifurcation reported earlier [7] 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 [11].

In short, judged by the frequency dependence of χ' below the peak as well as by distinct χ'' 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 χ' 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 χ'' feature at 2 K also rules out spin glass freezing for this composition.

We would like to mention that we have also measured [12] MR($= [\rho(H) - \rho(0)]/\rho(0)$) 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 40–60 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 χ 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 χ'' 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 χ' plots (Fig. 1). The additional spin-glass transition (around 2.5 K) seen in the ac χ data for the compositions $x =$ 0.0–0.3 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 $x = 0.1$–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 [13] 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 (summarized 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 realized only at the weak coupling limit, but not close to QCP, in contrast to the hitherto observed, predicted or assumed behavior [1–5]. 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.

Acknowledgements

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 Sarojini 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.

References

[1] M.B. Maple, M.C. de Andrade, J. Herrmann, Y. Dalichaouch, D.A. Gajewski, C.L. Seaman, R. Chau, R. Movshovich, M.C. Aronson, R. Osborn, J. Low Temp. Phys. 99 (1995) 314.
[2] J. Garcia Soldevilla, J.C. Gomez Sal, J.A. Blanco, J.I. Espeso, J. Rodriguez Fernandez, Phys. Rev. B 61 (2000) 6821.
[3] A.H. Castro Neto, et al., Phys. Rev. Lett. 81 (1998) 3531.
[4] A. Theumann, B. Coqblin, S.G. Magalhaes, A.A. Schmidt, Phys. Rev. B 63 (2001) 054409.
[5] M. Kiselev, K. Kikoin, R. Oppermann, arXiv:cond-mat/0106591.
[6] R.A. Gordon, C.J. Warren, M.G. Alexander, F.J. DiSalvo, R. Pöttgen, J. Alloys Compd 248 (1997) 24.
[7] S. Majumdar, E.V. Sampathkumaran, Phys. Rev. B 62 (2000) 8959.
[8] S. Doniach, Physica B 91 (1977) 231.
[9] R. Mallik, E.V. Sampathkumaran, M. Strecker, G. Wortmann, P.L. Paulose, Y. Ueda, J. Magn. Magn. Mater. 185 (1998) L135.
[10] J.A. Mydosh, Spin Glasses: An Experimental Introduction, Taylor & Francis, London, 1993.
[11] S.B. Roy, A.K. Pradhan, P. Chaddah, E.V. Sampathkumaran, J. Phys. Condens. Matter 9 (1997) 2465.
[12] S. Majumdar et al., Proceedings of the International Conference on Advances in Superconductivity and Magnetism, held in Mangalore, September 2001, Pramana-J. Phys. in press.
[13] L. Gondek, B. Penc, A. Szytula, S. Majumdar, E.V. Sampathkumaran, N. Stusser, J. Magn. Magn. Mater. (2002) in press.