

Magnetic anomalies in the pseudoternary alloy series $\text{Ce}_2\text{Co}_{1-x}\text{Au}_x\text{Si}_3$

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We report the results of heat-capacity, magnetization, and electrical resistance measurements down to 2 K for a solid solution $\text{Ce}_2\text{Co}_{1-x}\text{Au}_x\text{Si}_3$, forming in a crystal structure derived from AlB_2 -type hexagon. The results reveal that, at low temperatures, the magnetic ordering (setting in at a temperature below 8 K) dominates over the Kondo effect at the Au rich end, while the Kondo effect takes over for the Co rich end driving Ce_2CoSi_3 to nonmagnetism, with highest magnetic ordering temperature in this series for the composition range $x=0.8-0.9$. There appear to be dramatic changes in the magnetic structure with the variation of x , as well as with temperature (T) for some intermediate compositions in the magnetically ordered state, as inferred from the magnetization data. For those compositions ($x=0.9$ and 0.8) in which we observe double magnetic transitions as inferred from the heat-capacity data, field-cooled and zero-field-cooled magnetic susceptibilities deviate from each other for the lower- T (in the vicinity of 3–4 K) transition alone, as if the higher- T (around 7 K) transition is definitely not of a spin-glass type. These results, characterizing this solid solution as an interesting one, offer an opportunity to understand almost the entire range of Doniach's magnetic phase diagram in a single solid solution.

The magnetic properties of Ce alloys have been known to be controlled by a delicate balance between Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction and the Kondo effect. The competition between these two mechanisms has been viewed in the literature in light of Doniach's one-dimensional Kondo necklace model.¹⁻³ It is of constant interest to identify new solid solutions with magnetic anomalies due to the competition between these effects and the studies of Ce compounds crystallizing in ThCr_2Si_2 -type crystal structure have been the most common ones in this regard (see, for instance, Refs. 4–7). Here, we report the identification of a solid solution⁸ $\text{Ce}_2\text{Co}_{1-x}\text{Au}_x\text{Si}_3$, in which one is able to transform from strong Kondo regime to a RKKY-interaction-dominated regime traversing through a peak in magnetic ordering temperature (T_0) for the intermediate composition range with the variation of composition. A point of major emphasis is that, among these alloys, there are also qualitative differences in the isothermal magnetization (M) behavior, hysteresis loops and also in the shapes of heat-capacity (C) versus temperature (T) plots below T_0 ; in addition, for some intermediate compositions, the magnetic structure appears to get modified with decreasing T below T_0 . The results overall characterize that this pseudoternary series exhibits interesting magnetic properties.

The samples were prepared by melting together stoichiometric amounts of constituent elements in an arc furnace. The ingots were subsequently homogenized at 900 °C for six weeks in sealed evacuated quartz tubes and characterized by x-ray diffraction (Cu $K\alpha$). We notice that the diffraction patterns could be indexed to an AlB_2 derived structure as proposed earlier,⁸ except for $x=1.0$; for $x=1.0$, additional weak lines (marked by asterisk in Fig. 1) in the x-ray diffraction pattern appear, which can be assigned to a small amount of a tetragonal impurity phase; it is, however, worth noting that these extra lines can also be indexed if one proposes an orthorhombic structure for this composition alone, as proposed for Ce_2CuGe_3 very recently,⁹ with the lattice constants

$a=7.242$ Å, $b=5.086$ Å, and $c=4.086$ Å. A shorter annealing time, say for one week, enhances the presence of these extra lines for Au-rich end; all the results reported here are restricted to the long-annealed specimens only, except for $x=0.0$ and 0.2 , in which cases shorter annealing time does not result in appearance of these extra lines in the x-ray pattern. The observation of these additional lines for short-annealed samples is consistent with that of Gordon *et al.*⁸ The C data were collected by semiadiabatic heat-pulse method in the temperature interval 2–30 K. The magnetic susceptibility (χ) in a magnetic field (H) of 2 kOe in the T interval 2–300 K and isothermal M measurements at 2 and 5 K were performed for the zero-field cooled (ZFC) state of the specimens employing a superconducting quantum interference device (SQUID, Quantum Design) or a vibrating sample magnetometer (VSM, Oxford Instruments) (incidentally, the data obtained by both these instruments are found to agree within few percent). In addition, the ZFC and the field-cooled (FC) χ data below 15 K as well as hysteresis loops were obtained at 2 and 5 K for all the magnetically ordering compositions. The electrical resistance (R) measurements (1.4–300 K) were performed by a conventional four-probe method.

We first make few remarks about the crystallographic parameters with the indexing of the x-ray diffraction patterns to an AlB_2 -derived structure. It is not easy to infer on the doubling of the unit-cell dimensions with respect to AlB_2 unit cell, as the corresponding superstructure lines (100) and (110) in the diffraction patterns due to Co/Au/Si crystallographic ordering are so weak that it can escape detection. We have carefully tracked these lines to draw an inference in this regard. According to the present observation, the a axis is doubled in all cases, while the c axis is not, except for Ce_2AuSi_3 . (For $x=0$, $a=8.113$ Å and $c=4.219$ Å; for $x=1$, $a=8.306$ Å and $c=8.687$ Å.) These findings are broadly in agreement with that reported in Ref. 8, except for $x=0.6$ in which case the a parameter was not reported to

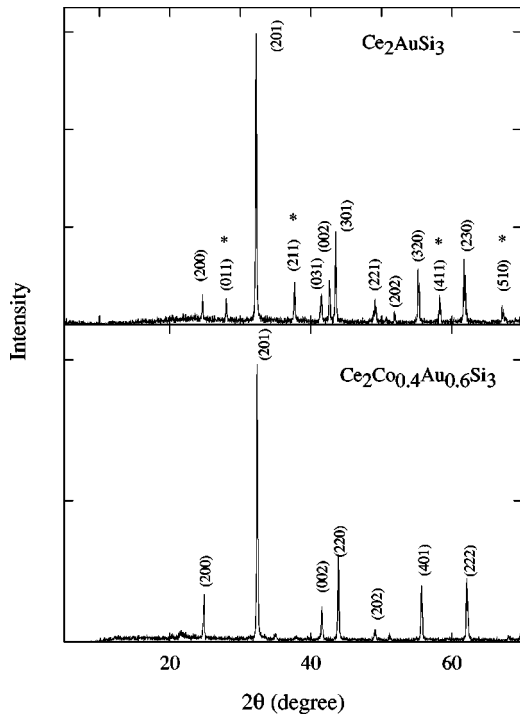


FIG. 1. X-ray diffraction (Cu $K\alpha$) for the alloys, $\text{Ce}_2\text{Co}_{1-x}\text{Au}_x\text{Si}_3$ ($x=0.6$ and 1.0) at 300 K to highlight the presence of additional lines for $x=1.0$, if interpreted in an AlB_2 -derived hexagonal structure. The Miller indices for intense lines are shown and for $x=1.0$ the indexing given are for orthorhombic structure. The asterisks mark the extra lines discussed in the text.

double earlier. For the purpose of looking for systematics in the variation of unit-cell volume (V) with x , if the doubling of unit-cell parameters is ignored and also assuming that the crystal structure for Ce_2AuSi_3 is the same as those of other compositions, we plot in Fig. 2 the x dependence of unit-cell parameters; it is clear that one observes monotonic variation of the lattice constants with an increase in V of about 8%, as one traverses from Co end to Au end. However, it appears

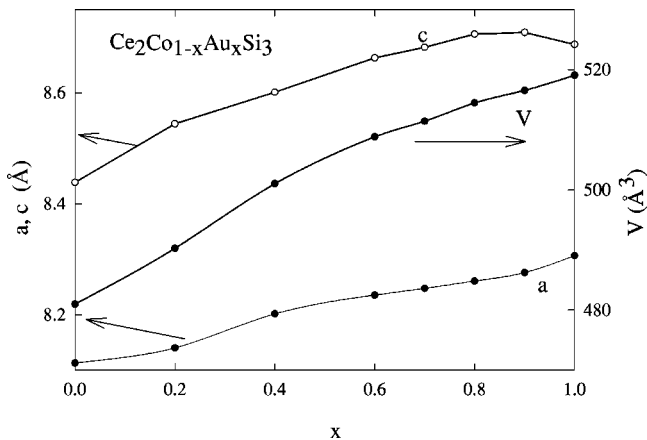


FIG. 2. The lattice constant, a and c and unit-cell volume V as a function of x in the series $\text{Ce}_2\text{Co}_{1-x}\text{Au}_x\text{Si}_3$, according to the indexing of the x-ray diffraction patterns to an AlB_2 -derived hexagonal structure. The lattice constant, c , shown in the plot is doubled in all cases except for $x=1.0$, for the sake of convenience. The lines through the data points serve as guides to the eyes.

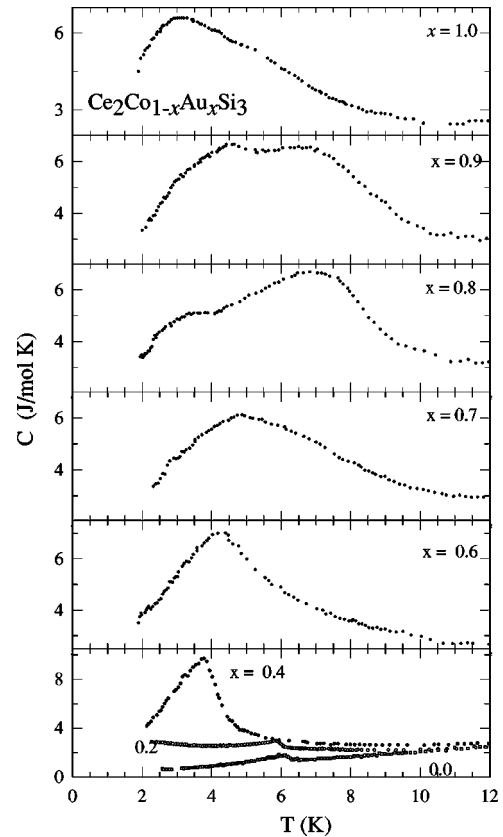


FIG. 3. Heat capacity as a function of temperature in the alloys $\text{Ce}_2\text{Co}_{1-x}\text{Au}_x\text{Si}_3$.

that the Vegard's law is not obeyed, which may be attributed to significant differences in the compressibilities of these alloys.

The T -dependent C behavior is plotted in Fig. 3 for all the compositions. The compound Ce_2CoSi_3 does not exhibit any feature attributable to long range magnetic ordering except for a small peak around 6 K presumably due to small amounts (close to 1%)¹⁰ of trivalent Ce oxide impurity phase, often reported in the literature to appear in many Ce alloys. However, it is clear that there are prominent features below 10 K in the plots as Au content is increased, attributable to magnetic ordering. For instance, for Ce_2AuSi_3 , there is a peak at 3.2 K, however with a tail extending up to about 10 K, either due to heavy-fermion character or due to magnetic precursor effects.^{11,12} There are apparent qualitative changes in the shapes of C versus T plots as x is varied. For $x=0.9$ and 0.8 , there are two peaks close to 4 and 7 K, respectively, as if there are two magnetic transitions, and the relative intensity of the 4 K peak is lower for $x=0.8$. For further lowering of Au content, say, for $x=0.7$, a broad feature with one peak at 4.7 K, and for $x=0.6$, a less broader peak at 4.2 K are seen. Interestingly, for $x=0.4$, the peak gets *narrowed down* with a consequent enhancement of the peak value at 3.8 K. From these findings, we infer that, for $x>0.6$, local environmental effects may play a dominant role on magnetism. If one tracks the T at which the C peaks with varying composition, then one can conclude that T_0 , generally believed to be close to this peak temperature,¹¹⁻¹³ undergoes a nonmonotonic variation with x ; this conclusion is qualitatively valid irrespective of which of the two peaks for

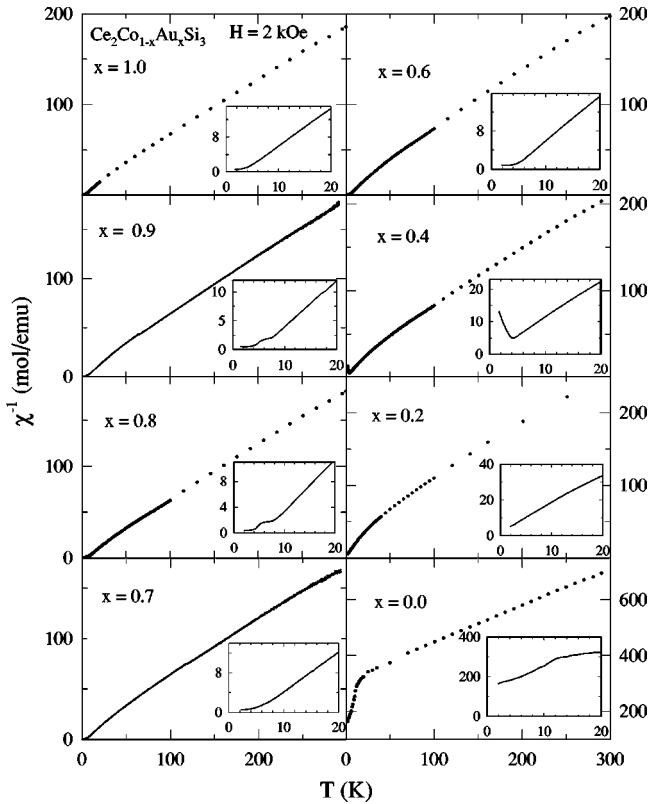


FIG. 4. Inverse susceptibility as a function of temperature in the alloys $\text{Ce}_2\text{Co}_{1-x}\text{Au}_x\text{Si}_3$. The low temperature behavior is shown in an expanded form in the inset to highlight qualitative changes in the χ behavior. Some of the data, for instance for $x=0.9$ and 0.7 , were collected by VSM, while most of the data were obtained by a SQUID magnetometer.

$x=0.8$ and 0.9 is tracked. We have also carried out C studies for $\text{Ce}_2\text{Co}_{0.8}\text{Au}_{0.2}\text{Si}_3$ from a different batch (annealed for a period of about one week, but single phased); we notice that there is no feature due to magnetic ordering above 2 K (except perhaps a tiny peak around 6 K attributable to the presence of about 1% of magnetic Ce oxide impurities). Thus, among the compositions studied, the magnetic ordering disappears for $x < 0.4$ above 2 K. The end Co member is a nonmagnetic heavy fermion¹⁰ with moderate values of linear coefficient of C . On the basis of these results, it may be stated that this alloy series spans a wide range in the Doniach's magnetic phase diagram, with the compositions $x=0.8$ and 0.9 lying at the peak position of this diagram. In support of this, we have also obtained the linear coefficient (γ) of C from the data in the range 10–20 K and the values (± 10 mJ/mol K²) are 70, 100, 118, 106, 110, 155, 120, and 125 mJ/mol K² for $x=1.0, 0.9, 0.8, 0.7, 0.6, 0.4, 0.2, 0.0$, respectively. We note that γ goes through a peak as expected for a series covering wide range of Doniach's diagram; the value peaks for $x=0.4$ among the compositions studied, which is expected for an alloy which is placed close to nonmagnetic-magnetic phase boundary.

In order to get more insight on the magnetic behavior of these alloys, we have carried out χ measurements. The plots of inverse χ versus T are shown in Fig. 4 and, for all the compositions, the plots are found to be linear above 100 K except for $x=0.0$; for Ce_2CoSi_3 , we have plotted the data

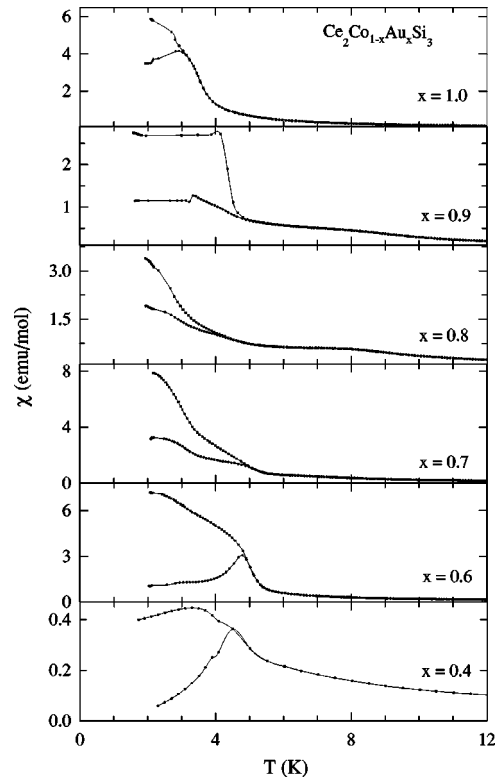


FIG. 5. The zero-field-cooled and field-cooled magnetic susceptibility behavior below 12 K in the alloys $\text{Ce}_2\text{Co}_{1-x}\text{Au}_x\text{Si}_3$ as measured by applying a magnetic field of 50 kOe. The lines through the data points serve as guides to the eyes.

after subtracting¹⁰ large T independent contribution in order to observe the high-temperature linear plot. The value of the effective moment derived from the high-temperature linear region is found to be very close to that expected for trivalent Ce ions within the limits of experimental accuracy; the values of the high-temperature paramagnetic Curie-Weiss parameter (Θ_p) are found to be $-15, -11, -8, -20, -30, -40, -50$, and -240 K for $x=1.0, 0.9, 0.8, 0.7, 0.6, 0.4, 0.2$, and 0.0 , respectively, thus undergoing a sharp variation for x below 0.4 . Considering that the values of T_0 are much lower compared to the magnitudes of respective Θ_p , we infer that the negative sign with a large magnitude arises from the Kondo effect. There is a distinct deviation from linearity (Fig. 4) typically below about 100 K due to crystal field effects. However, in sharp contrast to the finding at high temperatures, the low temperature (in the range 10–20 K) Θ_p is positive for all compositions beyond $x=0.2$ with the magnitudes falling in the range 1 to 6 K; for Co rich end, however, the sign is negative (-1 and -45 K for $x=0.2$ and 0.0 , respectively) (Fig. 2, inset). These findings indicate that, for a given composition, the strength of the Kondo interaction gets diminished as the T is lowered following crystal field effects; the positive sign of low temperature Θ_p for the Au-rich members even raise a question whether these alloys are truly low temperature Kondo systems.

There are various other noteworthy features in the shapes of the plots of low-temperature χ and M data of magnetically ordering alloys (Figs. 4, 5, 6, and 7). Turning to Fig. 4 (for the magnetic behavior in an applied H of 2 kOe), the tendency of χ to saturate below the T range of 4–5 K for $x=1.0, 0.9, 0.8, 0.7$, and 0.6 is typical of low-temperature ferromagnetic ordering; in addition for $x=0.9$ and 0.8 , we

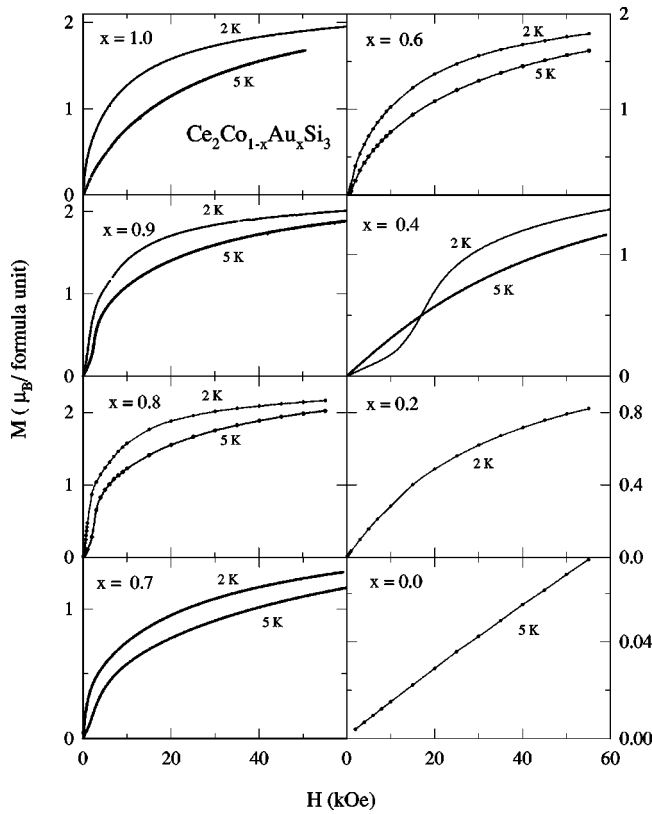


FIG. 6. The isothermal magnetization behavior at low temperatures for the alloys $\text{Ce}_2\text{Co}_{1-x}\text{Au}_x\text{Si}_3$. The continuous lines through the data points obtained by a SQUID magnetometer (for some cases) serve as guides for the eyes.

see additional shoulders around 7 K, indicative of another magnetic transition around this temperature. These shoulders are not seen for $x=0.7$ and 0.6 , as if the 7 K transition is absent for these compositions. Interestingly for $x=0.4$, there is a very prominent peak at about 4 K, as if this alloy orders antiferromagnetically unlike other compositions. There is no evidence for long range magnetic ordering above 2 K for $x=0.2$ in the χ data. The observed magnitudes/trends in the magnetic ordering temperature are broadly consistent with those inferred from the C data above and therefore these represent zero-field behavior. We have also probed ZFC and FC behavior of χ in low fields (50 kOe) for magnetically ordering specimens (Fig. 5); it is obvious that ZFC and FC χ deviate in the magnetically ordered state and it is at present not clear whether this deviation arises from spin-glass behavior, as similar feature has been known in alloys with long range magnetic ordering as well due to domain-wall pinning effects. However, it is to be noted that this deviation (for compositions with double magnetic transitions) occurs only for the low- T transition (in the vicinity of 3–5 K), but not for the high- T transition (appearing as a very broad peak around 7 K for $x=0.8$ and 0.9 even in the low field data). This finding establishes that the 7 K transition definitely is not of a spin-glass type.

The interesting conclusion on the changeover in the magnetic structure as x is varied (as inferred above) gains support from the isothermal M data at 2 and 5 K as well, shown in Fig. 6. For $x=1.0$, M tends towards saturation (though not completely at high fields) with the application of H at 2 K;

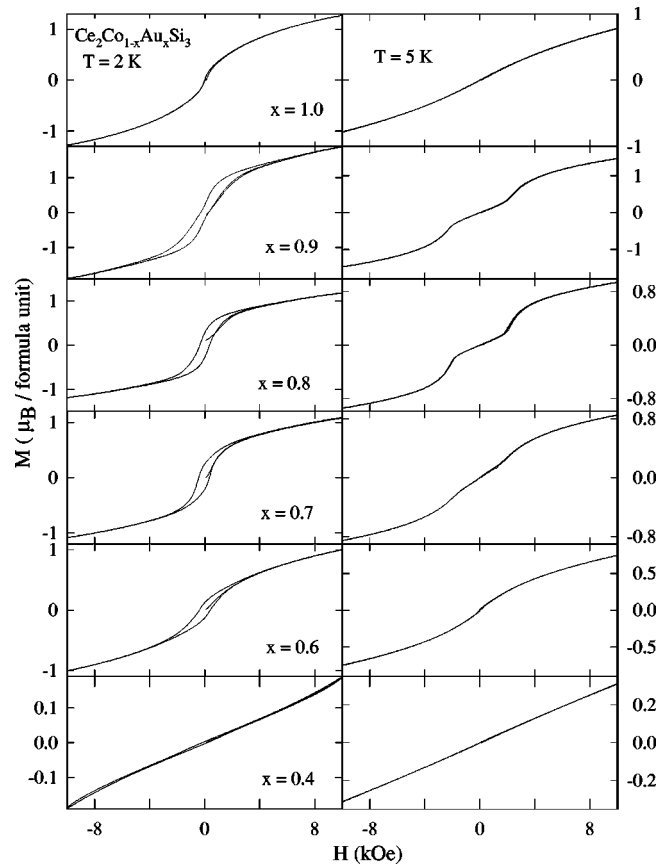


FIG. 7. Hysteresis loops at 2 and 5 K (left and right respectively) for magnetically ordering alloys of the series, $\text{Ce}_2\text{Co}_{1-x}\text{Au}_x\text{Si}_3$.

the value of the saturation magnetization (M_{sat}) extrapolated from high H to zero H , is about $0.8\mu_B$ per Ce very close to that expected for doublet ground state of Ce. For $x=0.9$ and 0.8 , the 5 K data show the existence of a metamagnetic transition at low fields (close to 2 kOe, see also Fig. 7); however, at 2 K, there is a smooth (but comparatively steeper) rise till about 20 kOe without any evidence for metamagnetism. This finding is taken to indicate that, in zero field, there appears to be a transformation from a magnetic structure in which antiferromagnetism dominates towards ferromagnetism with decreasing T in the magnetically ordered state in these two compositions. The alloy with $x=0.7$ also exhibits somewhat similar behavior. For $x=0.6$, the features in the plots resemble that of the parent Au compound, however, with a difference in hysteresis loop at 2 K (see Fig. 7) in the sense that the former exhibits hysteretic isothermal magnetization behavior. The M versus H plot in the magnetically ordered state (at 2 K, but not at 5 K) for $x=0.4$ exhibits a very pronounced metamagnetic transition, however, without any significant hysteretic behavior, at relatively higher fields (around 15 kOe), as if the low field (<10 kOe) state is antiferromagneticlike, a finding in conformity with the conclusion from the χ versus T plot; the plot of M vs H is linear below 8 kOe at 2 K (Fig. 6), unlike the observation in other magnetically ordering compositions. Thus the results reveal interesting changes in the magnetic structure both as a function of composition as well as of temperature in this pseudoternary series. Further evidence for this conclusion can be obtained from the nature of hysteresis curves at 2 and 5 K

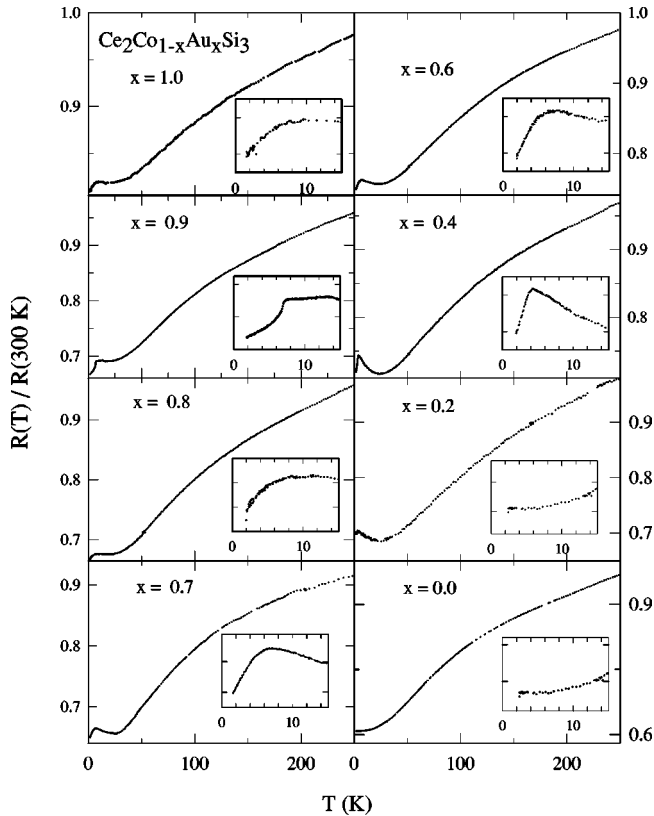


FIG. 8. The electrical resistance R (normalized to respective 300 K values) as a function of temperature in the alloys $\text{Ce}_2\text{Co}_{1-x}\text{Au}_x\text{Si}_3$. Insets show the low-temperature profile of R in an expanded form in order to highlight the features due to magnetic ordering.

(Fig. 7) by sweeping H in the range $+10$ to -10 kOe (starting with zero H , H was increased to 10 kOe, then decreased to -10 kOe and finally increased back to $+10$ kOe); at 2 K, while the loop is closed for $x=0.0$, all the compositions with $x<0.4$ exhibit open loops; the absence of a loop for $x=0.0$ alone is surprising, which may indicate that, if it is ferromagnetic, it is of a soft type; also interesting to note is that the loop is absent at 5 K for all compositions and this observation particularly for $x=0.9$ and 0.8 combined with metamagnetic transitions around 2 kOe is an evidence in favor of an antiferromagneticlike magnetic structure in zero fields at 5 K, thereby establishing the points made above. Few other observations in the plot of isothermal M data are (i) we do not see complete saturation of M even at high fields in any of the compositions. The value of M_{sat} gets reduced for increasing substitutions of Co for Au. The absence of the saturation, very prominent for some intermediate compositions, and the reduced values of M_{sat} (about $0.4\mu_B$, for instance, in $x=0.4$) may also be alternatively attributed to possible itinerant magnetism in these alloys due to some degree of $4f$ delocalization; however, we are not able to forcefully advance this explanation, as there is no way that we could exclude possible presence of some fraction of Ce ions in the paramagnetic state at such low temperatures due to local environmental effects or to possible competition from antiferromagnetism even at high fields. (ii) For $x=0.2$, M exhibits nonlinear variation with H at 2 K, as if Ce ions are on the verge of undergoing magnetic ordering thereby implying that

T_0 for this alloy may be just below 2 K. (iii) The metamagnetic transitions observed for some compositions are found to be nonhysteretic.

We have also measured electrical resistance behavior as a function of T . The resistivity value at 300 K is typically of the order $200 \mu\Omega \text{ cm}$ and there are difficulties in looking for systematics in absolute values due to microcracks in the samples. R exhibits an observable drop in the vicinity of respective T_0 in all the magnetically ordering specimens (Fig. 8). However, the temperature at which the drop begins is few degrees more (Fig. 8, inset) than the actual magnetic ordering onset temperatures inferred from the C data for $x=1.0$ and 0.6 . This is not surprising, considering that, in some of magnetically ordering systems, short range correlation effects can give rise to such a magnetic precursor effect. Thus the R data sometimes are not useful to look for systematics in T_0 within a given series of alloys. The point of main emphasis is that, above T_0 , there is no prominent minimum for the Au-rich end, as if the single-ion Kondo effect is negligible at low temperatures for $x>0.4$. This observation may endorse the inference drawn from the positive sign of low-temperature Θ_p data discussed above. We have in fact prepared several compositions of the series, $\text{Ce}_{2-x}\text{La}_x\text{AuSi}_3$, and measured R as a function of T down to 1.4 K and we do not find a R minimum even in the dilute alloys [unlike the situation in $\text{Ce}_{2-x}\text{La}_x\text{CoSi}_3$ (Ref. 10)], thus establishing negligible role of the Kondo effect in this chemical environment. The appearance of the Kondo minimum with decreasing Au content is gradual and a well-defined minimum at about 25 K for $x<0.6$ is observable. For the end Co member, no minimum is expected due to Kondo coherence effects with a large Kondo coherence temperature.¹⁰

To summarize, while the compound, Ce_2CoSi_3 , is a non-magnetic Kondo-lattice compound, the present results reveal that the end Au compound magnetically orders close to 4 K with negligible role of Kondo effect at such low temperatures. The gradual replacement of Au for Co results in the onset of magnetic ordering at a temperature well beyond that in Ce_2AuSi_3 and the value of T_0 is maximum for the composition range $x=0.8-0.9$ (at 7 K) judged by the features in C , thus placing this composition range at the peak of Doniach's magnetic phase diagram, if viewed in light of Doniach's model. For intermediate compositions, say around $x=0.4$, the features due to both magnetic ordering and the Kondo effect in the R data appear, unlike the situation for two extreme end members. This solid solution thus apparently covers a wide spectrum in Doniach's magnetic phase diagram. The nature of the magnetic structure appears to undergo interesting modifications with the variation of x , and also as a function of T in some cases, as inferred from the magnetization data. Thus, the transformation from magnetism to the Kondo effect with x is not found to be a gradual one in finer details at low temperatures in the solid solution $\text{Ce}_2\text{Co}_{1-x}\text{Au}_x\text{Si}_3$. The observed features are interesting, considering that, in the simple-minded picture of Doniach's magnetic phase diagram, one does not anticipate such major changes in the magnetic structure both as a function of T as well as of unit-cell volume. We attribute these anomalies to the combined effect of *large* changes both in unit-cell volume and the electronic structure following chemical substitution. Finally, it is worthwhile to carry out further low-

temperature studies for alloys with x below 0.2, at the magnetic-nonmagnetic phase boundary, to look for non-Fermi-liquid characteristics. It is also worth pursuing neutron diffraction studies for all the compositions to understand the

changes in the magnetic structure as well as to refine crystal structure as a function of composition and temperature, particularly to clarify whether some of the compositions exhibit spin-glass ordering.

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