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VARIATION OF GROUND STATES IN $CePt_{2-x}Au_xSi_2$ COMPOUNDS (x = 0, 1, 2)

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A comparison is made of some low-temperature properties of $CePt_2Si_2$, $CePtAuSi_2$ and $CeAu_2Si_2$. New experimental data on the specific heat, electrical resistivity and magnetic susceptibility of $CePtAuSi_2$, together with published results on the other compounds, reveal that the electronic ground state in these materials varies in a very significant way. In-between local-moment behaviour in $CeAu_2Si_2$ and a Kondo-type ground state in $CePt_2Si_2$, $CePtAuSi_2$ forms a heavy-electron state at low temperatures.

Most CeM_2Si_2 compounds, with M as a *d*-transition metal, crystallize in the $ThCr_2Si_2$ structure[1]. Some of them are known for their particular low-temperature properties. The most spectacular features are observed in $CeCu_2Si_2$, a heavy-electron superconductor[2], and in $CeRu_2Si_2$, which adopts a heavy-electron ground state without a phase transition down to 0.1 K. At low temperatures this state is unstable in high magnetic fields as evidenced by a metamagnetic-type transition[3,4]. A replacement of Ce by La in $CeRu_2Si_2$ appears to induce a magnetically ordered ground state below 10 K [3].

Various unusual features are observed in compounds where M is a 5*d* transition element. In $CeOs_2Si_2$ the 4*f* electrons appear to be delocalized in spite of a fairly large Ce–Ce interatomic distance of 4.162 Å [5], whereas in $CePt_2Si_2$ a well-defined local moment of the 4*f* electron is indicated by a Curie–Weiss-type temperature dependence of the magnetic susceptibility $\chi(T)$ at temperatures above 200 K [6], but no magnetic order has been observed above 0.3 K [7]. $CeOs_2Si_2$ crystallizes in the $ThCr_2Si_2$ structure[5] while $CePt_2Si_2$ instead adopts the $CaBe_2Ge_2$ structure[6]. If Pt is replaced by Au, the resulting compound $CeAu_2Si_2$ is again a member of the $ThCr_2Si_2$ family and its local-moment behaviour is evidenced by a magnetically ordered state at low temperatures[8-10]. In view of these features, it seemed of interest to study the influence of a partial replacement of Pt by Au on the low-temperature behaviour of this type of compound.

In this report we compare some low-temperature properties of $CePt_2Si_2$, $CePtAuSi_2$ and $CeAu_2Si_2$. To this end we measured the specific heat $C_p(T)$ of $CePtAuSi_2$ and $CeAu_2Si_2$ between 0.1 and 30 K, and between 1.5 and 20 K, respectively. In addition we present new results of resistivity $\rho(T)$ and susceptibility $\chi(T)$ measurements on $CePtAuSi_2$ between 1.5 K and room temperature. Analogous data for $CePt_2Si_2$ and $CeAu_2Si_2$ are cited from the literature. The preparation of the samples was done in the same way as described in ref. 6. As these compounds crystallize easily from the melt, the samples contained rather large crystallites, so that the observed physical properties may be influenced by preferred orientation of the grains. Our x-ray analysis revealed that $CePtAuSi_2$ adopts the same structure as $CePt_2Si_2$ (see above). On this level of detectability, Pt and Au appear to be distributed homogeneously throughout the sample.

In Fig. 1 we show the temperature dependence of the specific heat $C_p(T)$ of $CeAu_2Si_2$ between 1.5 and 17.5 K. The data above 10 K can be fitted very well with a sum of the type $C_p = \gamma T + \beta T^3$, where $\gamma = 2.7$ mJ/mole K^2 and $\beta = 1.165$ mJ/mole K^4. The latter value is compatible with a Debye temperature $\theta_D = 203$ K, and the low γ value indicates that the conduction electrons have little or no *f* character. After subtraction of this "background specific heat" we are left with the magnetic part of $C_p(T)$, which is also shown in Fig. 1. The resulting anomaly manifests the previously reported magnetic ordering[10] and its shape is very close to what is expected for a simple mean-field-type transition. Nevertheless, some contribution from critical behaviour above $T_N = 7.3$ K appears to be present. The Néel temperature that we find here is in-between two previously published values of 6 K [8] and 10 K [9,10].

Although the phase transition to a magnetically ordered state of $CeAu_2Si_2$ seems to vary in temperature

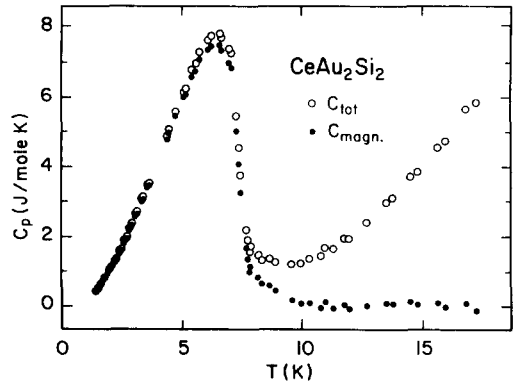

Fig. 1 - Temperature dependence of the specific heat of $CeAu_2Si_2$ between 1.5 and 17 K. Open circles denote the total specific heat, solid circles are obtained by subtracting of the contributions due to conduction electrons and the lattice (see text).

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between different materials, the low-temperature behaviour of this compound is close to classical expectations, as we shall outline below. According to ref. 9 the temperature dependence of χ below room temperature is well described by a Curie–Weiss law with a negative paramagnetic Curie temperature θ_p = -12 K. The resulting effective moment is 2.57 μ_B/Ce coinciding with the value that is expected for non-interacting Ce^{3+} ions. Although no distinct features for crystal-electric-field (CEF) effects are discernible in the $\chi^{-1}(T)$ data of ref. 9, it is expected that the Hund's rule J = 5/2 ground state is split and for symmetry reasons a ground-state doublet is expected. This is nicely confirmed by the value of the molar entropy involved in the experimentally determined magnetic anomaly shown in Fig. 1, which amounts to R ln2 within a few percent between 0 K and T_N. From neutron-scattering work reported in ref.10, a simple antiferromagnetic structure of type I was deduced and the ordered moment per Ce ions was found to be 1.3 μ_B/Ce, a value that may well correspond with possible wave-functions of the lowest doublet state.

The low-temperature magnetic susceptibility of $CePt_2Si_2$ is distinctly different from that of $CeAu_2Si_2$. As described in refs. 6 and 7, only at elevated temperatures above 200 K is a Curie–Weiss-type behaviour observed. With decreasing temperature, $\chi(T)$ reaches a maximum around 60 K and after a subsequent decrease is approximately constant below 20 K. These unusual features for a Ce compound are absent in $CeAuPtSi_2$. We show the result of our measurement in the form of a $\chi^{-1}(T)$ plot in Fig. 2.

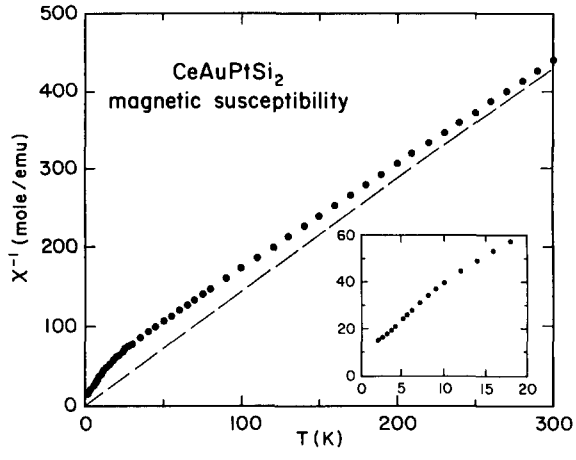

Fig. 2 - $\chi^{-1}(T)$ between 1.5 and 300 K for polycrystalline $CePtAuSi_2$. The broken line indicates a possible underlying Curie–Weiss susceptibility that is changed by crystal-field effects to give the experimental data. The inset emphasizes the temperature range below 20 K.

We note that the data between 30 and 300 K are fitted very accurately by a straight line, implying a $(T - \theta_p)^{-1}$ dependence of χ. At lower temperatures $\chi(T)$ increases more rapidly with decreasing temperature. The inset of Fig. 2 emphasizes the behaviour below 20 K. The most probable cause for the particular shape of the $\chi^{-1}(T)$ curve are crystal-field effects. A possible underlying Curie–Weiss behaviour, as indicated by the broken line in Fig. 2, is altered by the thermally induced change of occupation of the CEF-split 4f-electron levels, again 3 doublet states in this case. The resulting effective moment is then about 2.4 μ_B/Ce and the paramagnetic Curie temperature negative but close to zero. Below 10 K another region of Curie–Weiss behaviour with again a small value for θ_p may be identified. With this interpretation the effective moment of 1.6 μ_B/Ce would have to be ascribed to the ground-state doublet.At the lowest temperatures a tendency towards saturation of $\chi(T)$ may be inferred from the experimental data.

In Fig. 3 we show the field dependence of the magnetization $M(H)$ for $CePtAuSi_2$ at a low temperature (2 K) and in fields up to 100 kOe. Here, a distinct difference to analogous results for $CeAu_2Si_2$, which were reported in ref. 9, have to be noted. Because of the

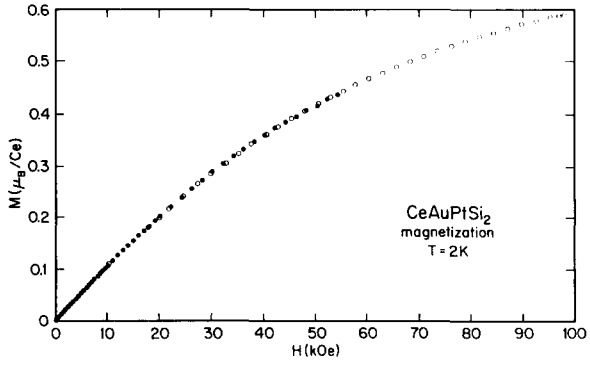

Fig. 3 - Magnetization versus external magnetic field for polycrystalline $CePtAuSi_2$ at 2 K up to 100 kOe. Solid circles were measured with a SQUID magnetometer and open circles were obtained using a moving-sample apparatus.

antiferromagnetic order in the latter compound, the field-induced transition to the paramagnetic state between 60 and 80 kOe leads to an s-shaped curve in that case. Although our maximum field value is 100 kOe, it is difficult to estimate a saturation value for M. Also for $CeAu_2Si_2$ this limit was by far not reached even in fields of 210 kOe [9], but our data on $CePtAuSi_2$ seem to extrapolate to roughly the same $M(H)$ values for H > 100 kOe.

The most intriguing differences in the low-temperature behaviour of the three compounds are apparent in the temperature dependences of the specific heat. In Fig. 4 we show, on a double-logarithmic diagram, our results for $C_p(T)$ of $CePtAuSi_2$ between 0.1 and 30 K, in comparison with data for $CePt_2Si_2$ reported in ref. 7. Fig. 5 shows the same data on a C_p/T vs. T plot for temperatures below 10 K. For temperatures between 4 and 10 K, Ayache and collaborators[7] fitted their data for $CePt_2Si_2$ with a sum of an electronic and a Debye-type lattice contribution, whereby the electronic specific-heat parameter γ= 86 mJ/mole K^2 and θ_D = 215 K. An analogous analysis of the data of

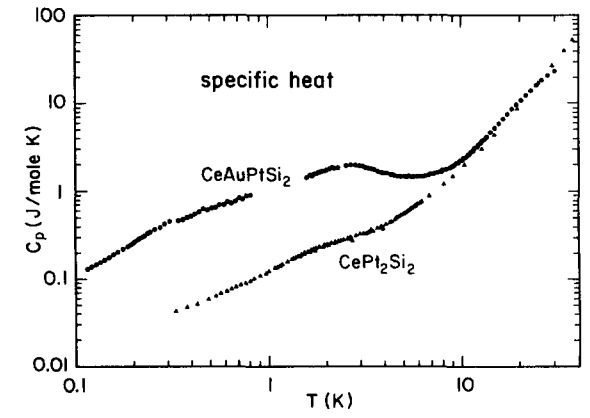

Fig. 4 - Specific heats of $CePt_2Si_2$ and $CeAuPtSi_2$ at low temperatures. Circles are due to this work and the triangles were taken from ref. 7.

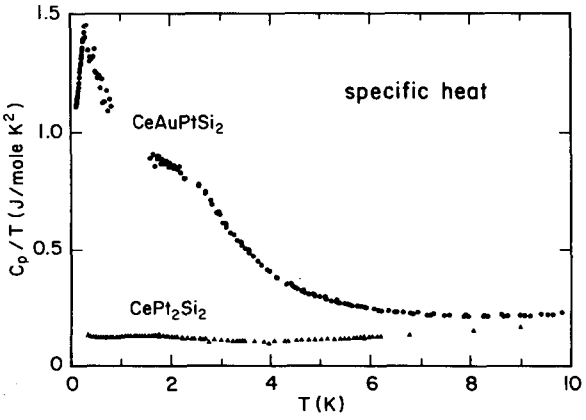

Fig. 5. - C_p/T versus temperature for $CePt_2Si_2$ and $CePtAuSi_2$ below 10 K, as derived from the data shown in Fig. 4.

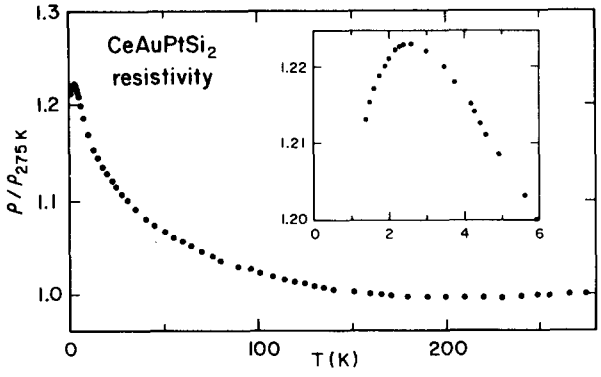

Fig. 6. - Temperature dependence of the electrical resistivity of polycrystalline $CePtAuSi_2$ between 1.3 and 275 K in units of the value ρ (T = 275 K). The inset emphasizes the temperature range below 6 K.

$CePtAuSi_2$ above 10 K leads to the values γ= 118 mJ/mole K^2 and θ_p = 212 K. Comparing, in particular, the values for the Debye temperatures for all three compounds we note that their lattice excitation spectra must be nearly identical. Therefore, the visible strong differences in $C_p(T)$ at low temperatures have to be due to variations in the electronic spectrum.

As we pointed out above, $CeAu_2Si_2$ behaves like a classical metallic rare-earth antiferromagnet where the exchange interaction mediated by the conduction electrons is the dominating factor for the low-temperature behaviour. The electronic structure must be quite different for $CePt_2Si_2$, as indicated by the unusual temperature dependence of χ. Its low-temperature electronic specific heat has indeed been interpreted as the lower end of a single-ion Kondo anomaly with a Kondo temperature of approximately 70 K [7].

The situation is again drastically different for $CePtAuSi_2$ where, at temperatures above 10 K, the electronic specific heat is larger but comparable in magnitude to that of $CePt_2Si_2$. Below 10 K, however, a strong enhancement of the C_p/T ratio in the Au-doped compound signals the formation of a heavy-electron state. With decreasing temperature, this enhancement appears to saturate but below 1 K a further enhancement and a maximum at approximately 0.3 K are observed. Extrapolating to T = 0, the C_p/T ratio seems to approach a value of roughly 1 J/mole K^2. After subtracting the lattice contribution to $C_p(T)$, the entropy of the heavy electrons can be evaluated and it reaches the value of R ln2 at approximately 20 K.

As a last item, we compare the electrical resistivity $\rho(T)$ of these three compounds at temperatures below 300 K. In Fig. 6, the temperature dependence of ρ for $CePtAuSi_2$ is shown between 1.3 and 280 K. For $CeAu_2Si_2$, analogous data were reported by Murgai and coworkers[9]. In this latter case, ρ decreases with decreasing temperature below 300 K. A few Kelvin above T_N, $\partial\rho/\partial T$ changes sign and the magnetic ordering manifests itself by a distinct chromium-type anomaly and a maximum in $\rho(T)$ just below the ordering temperature. With further decreasing T, $\rho(T)$ again decreases in the usual fashion of vanishing spin-disorder scattering. For $CePt_2Si_2$, ρ first increases with increasing negative slope on lowering T, passes through a maximum at about 70 K, and subsequently decreases considerably towards lower temperatures[6,7]. The maxima, both in $\chi(T)$ and $\rho(T)$ for this compound at almost the same temperature, were interpreted as a sign for the increasing dominance of a Kondo-type interaction and concomittant coherence effects among conduction electrons affecting the electronic transport[7].

For $CePtAuSi_2$, $\rho(T)$ passes through a shallow minimum around 200 K and, with decreasing temperature, increases with increasing negative slope. At temperatures below 4 K, we note a distinct maximum and a subsequent drop in ρ below $T_{max} \sim 2.5$ K. These features are very similar to those observed in other heavy-electron compounds, although for most other prominent Ce compounds in this class of substances, the onset of coherence or, in other words, a considerable decrease of ρ with decreasing temperature, is usually observed at distinctly higher temperatures such as about 10 K for $CeCu_6$ or 35 K for $CeAl_3$ [11].

The change of crystal structure between the two compounds $CePt_2Si_2$ and $CeAu_2Si_2$ is by itself an interesting feature. Clearly also the importance of different types of electronic interactions is varying distinctly from one substance to the other. Replacing Pt with Au leads to a decrease of the Kondo-type interaction, leaving it strong enough, however, to prevent the onset of cooperative magnetic order in the usual sense in $CePtAuSi_2$. The onset of a heavy-electron state in such compounds is obviously not restricted to materials crystallizing with the $ThCr_2Si_2$ structure, as we outlined above. Nevertheless, microscopic studies may reveal that, as in other substances[12], some unusual magnetic coherence occurs in this state possibly also in the case of $CePtAuSi_2$. It is especially the temperature dependence of the C_p/T ratio below 1 K which leads us to this conjecture. Unfortunately, these data are not compatible with a duplicate of the well known ground state of $CeCu_2Si_2$ [2] and the present experimental situation also gives no real clue for causes that determine the instabilities of heavy-electron states. In spite of this, further experiments on other materials with varying Pt to Au ratio, seeking the boundary of the crystal-structure change and investigating its influence on the magnetic behaviour might still be rewarding.

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