Solid State Communications, Vol.49, No.10, pp.955-958, 1984
Printed in Great Britain.

0038-1098/84 $3.00 + .00
Pergamon Press Ltd.

AN ELECTRONICALLY-DRIVEN VOLUME TRANSITION IN $CeSi_{2-x}Ga_x$

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(Received 1 December 1983 by J. Kanamori)

The pseudobinary compounds $CeSi_{2-x}Ga_x$ were prepared, and the lattice parameters and the susceptibilities were measured. At the Si-rich end, $0 \leq x < 0.2$, the system behaves as one with a high ($\sim$200K) Kondo temperature exhibiting no magnetic order. For $0.5 < x \leq 1.3$, the system shows the unit-cell volume 3% larger and orders ferromagnetically around 10K. The α-$ThSi_2$ structure is retained up to x=1.3, but one observes a two-phase region for $0.2 \leq x \leq 0.5$, consisting of small- and large-volume phases. This volume transition is magnetically one of the most drastic compared to previously studied Ce-based pseudobinaries.

Ce in its elemental form exhibits two distinct phases depending on pressure and temperature; a high-volume local-moment γ-phase and a low-volume Pauli-paramagnetic α-phase.[1] Both have the fcc structure and they convert to each other with a first-order transition. There have been efforts to induce a similar transition in Ce-based alloys and compounds by alloying instead of applying external pressure. Early examples are Ce_xTh_{1-x}[2] and $Ce_xLa_{1-x}Pd_3$.[3,4] In $Ce_xLa_{1-x}Pd_3$, they find an α-like phase at the Ce-rich side and a γ-like phase at the La-rich side, separated by a two-phase region extending between x=0.3 and 0.5. Another pseudobinary system receiving current interest is $Ce_xSc_{1-x}Al_2$,[4,5] in which two-phase behavior is observed at $x \lesssim 0.4$ but a rapid quenching technique stabilizes a nearly pure low-volume α-like phase. Corroborative evidence for a drastic change in the 4f-state near x=0.4 comes from neutron scattering.[6] We present here a new system, $CeSi_{2-x}Ga_x$, which shows a transition similar in nature to the above materials but has some different aspects because it is the non-rare earth that is substituted.

The tetragonal intermetallic compound $CeSi_2$ shows various anomalies associated with antiferromagnetic coupling of the 4f and conduction electrons[7,8]; the T-linear term in specific heat is very large, $\gamma = 104\,mJ/mole \cdot K^2$, and the susceptibility curve shows a significant deviation from the Curie-Weiss law for a tripositive Ce ion, reaching a finite value as $T \to 0$. Further investigations in the Ce-Si system[9] revealed that, even when the vacancies at the Si sites reach 15%, we have the α-$ThSi_2$ lattice in which $CeSi_2$ crystallizes. In addition, the magnetism of $CeSi_{2-x}$ displays a marked change with increasing x. The susceptibility is gradually enhanced with increasing x, and, for $0.17 \lesssim x \leq 0.3$, we observe an onset of ferromagnetic order with a reduced moment and reduced degrees of freedom presumably due to the Kondo effect. Recent resistivity measurements on single crystal $CeSi_{1.86}$ supports this picture.[10]

The stability of the lattice with such an amount of vacancies is rather amazing. We were motivated therefore to study the phase stability and the magnetic properties of $CeSi_{2-x}M_x$ (M=metallic element). The first candidate for M was a trivalent element Ga. The hexagonal $CeGa_2$(AlB_2-type), in contrast to $CeSi_2$, exhibits no dense Kondo complexities in its properties[11,12]; it shows a normal Curie-Weiss susceptibility expected for a tripositive Ce ion, eventually ordering antiferromagnetically at about 10K, and the resistivity shows no Kondo-like anomaly.

All samples studies here are polycrystals obtained by melting the constituents in an arc-furnace under a pure Argon atmosphere. Starting materials are Ce, La (better than 3N), Si and Ga (better than 5N). $CeSi_2$ and $CeGa_2$ were first formed and then appropriate proportions of them were melted to obtain the pseudobinary $CeSi_{2-x}Ga_x$. Both $CeSi_2$[13] and $CeGa_2$[14] form congruently and they were found to be single phase without further heat treatment; hence, the results reported here are on as-cast samples unless noted otherwise. The $LaSi_{2-x}Ga_x$ samples were prepared by the identical procedure. Samples were examined by the powder X-ray method.

We show in Fig.1 the Ga concentration dependence of the room temperature lattice parameters, a and c, for $CeSi_{2-x}Ga_x$ in the α-$ThSi_2$ structure. The striking feature is the coexistence of two isostructural phases extending over the interval $0.2 \lesssim x \lesssim 0.5$.

The changes in a and c, $\delta a/a$ and $\delta c/c$, accompanying the discontinuous transition are, respectively, 1.2% and 0.7%, resulting in a volume change $\delta V/V = 3.1\%$. Further check was provided with a diffractometer. For samples with x=0.2 and x=0.5, the respective minority phase appears as very weak, barely discernible shoulders by the peaks of the majority phase, which indicates that our assignment of the Ga concentrations at which the two-phase region terminates is fairly accurate. Furthermore, at x=0.3, a point dividing the two-phase region in the ratio 1:2, the sample showed intensities of a particular reflection roughly in the ratio 2:1 for the small-volume and the large-volume

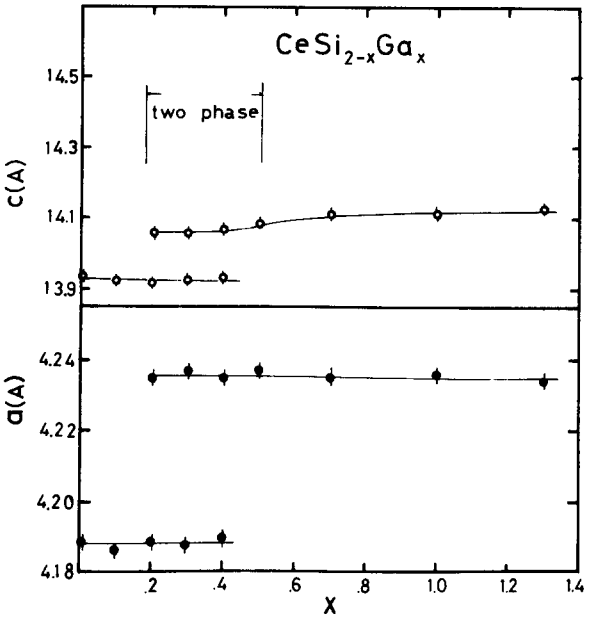

Fig.1 The lattice parameters, a and c, as a function of the Ga concentration for $CeSi_{2-x}Ga_x$ at room temperature.

phases. This suggests that we are observing a quasi-equilibrium phase diagram. No detectable change was observed in the lattice parameters or the two-phase behavior after annealing at 800°C for 3 days.

In the light of the previous work on Ce and its intermetallics mentioned in the introduction, we are inclined to believe that the abrupt volume change observed is related to the change in the 4f electron state. To check this conjecture, we also examined the lattice parameter behavior of $LaSi_{2-x}Ga_x$ where no 4f electron is present. We show the result in Fig.2. As seen in the figure, the variations of a and c are smooth with the Ga concentration x. A nonmonotonic variation of a is not uncommon in

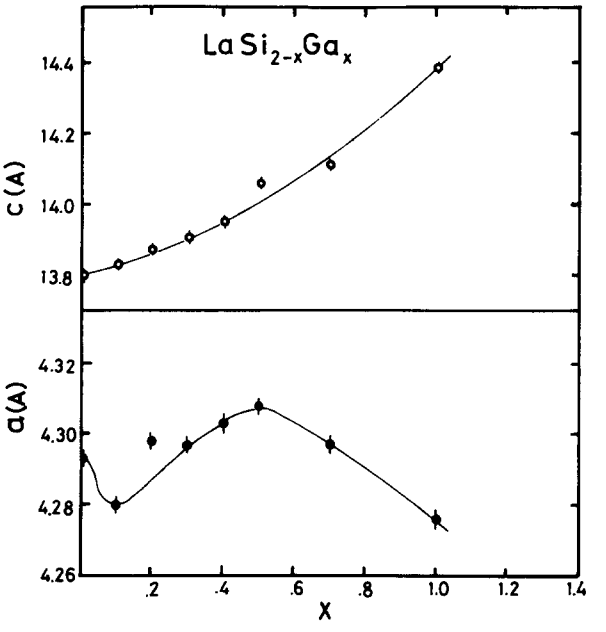

Fig.2 The lattice parameters, a and c, versus the Ga concentration for $LaSi_{2-x}Ga_x$ at room temperature.

structurally-related pseudobinaries.[15] At any rate, we do not observe a discontinuous volume transition of the type found in $CeSi_{2-x}Ga_x$. We note incidentally that the volume difference between the small-volume and large-volume phases for $CeSi_{2-x}Ga_x$, 3.1%, is close to the values found in $Ce_xSc_{1-x}Al_2$ and $Ce_xLa_{1-x}Pd_3$[4]. Except for the slight increase of c with x for $x \gtrsim 0.5$, the lattice parameter variations in the homogeneous regions are negligibly small, as seen in Fig.1. This is a feature not shared by $Ce_xSc_{1-x}Al_2$ or $Ce_xLa_{1-x}Pd_3$. The question of the homogeneity range retaining the α-$ThSi_2$ lattice was not pursued any further than x=1.3, where the sample still showed no indication of an extraneous phase.

The susceptibility of $CeSi_{2-x}Ga_x$ was measured in the temperature interval of 4.2 to 300K, and the results are shown in Fig.3. We note that the susceptibility, χ, increases appreciably with 5% Ga at low temperatures. The expanded phase samples with x=0.7, 1.0 and 1.3 show the χ behavior close to that of a tripositive Ce ion at higher temperatures (T>80K) and show magnetic order around 10K. The diverging behavior of χ around 10K indicates ferromagnetic order. As for the two-phase samples, we presume that only the expanded phase with $x \simeq 0.5$ participates in the divergence of χ.

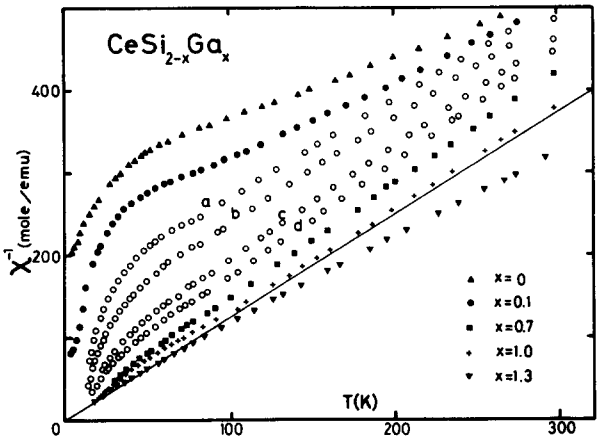

Fig.3 The inverse paramagnetic susceptibilities for $CeSi_{2-x}Ga_x$. The results for the two-phase samples are plotted with circles (a; x=0.2, b;0.3, c;0.4, d;0.5). The straight line is the Curie law for a tripositive Ce ion.

At higher temperatures, T>80K, the χ for the expanded phase approximately follows a Curie-Weiss law, $\chi^{-1}=(T+\Theta)/C$, with $\Theta \lesssim 10$K. This makes a clear contrast to the χ of $CeSi_2$, for which the above fit can be applied only at T>150K, giving $\Theta \simeq 350$K. The measurements by Dijkman et al.[8] in the higher temperature region, 200 to 600K, gave Θ=220K. The anomalously large Θ cannot be attributed to ordinary antiferromagnetic coupling between moments since the material remains paramagnetic down tc 0.1K.[7,16] Combined with other evidence mentioned in the introduction, we can seek its origin in the spin fluctuation due to the Kondo effect. A rough measure of the characteristic temperature, T_K, is given by the relation $\alpha T_K=\Theta$ ($\alpha=2\sim4$).[17] This gives T_K of order 100K for $CeSi_2$. Although this estimate involves ambiguities arising from the crystal field effect and the exchange interaction, it is supported by other estimates[9]; the T^2 coefficient of susceptibility gives 89K while the T-linear specific heat term gives 132K for T_K. In the expanded phase, the obtained values, Θ=5.5K both for x=0.7 and 1.0 and Θ=13K for x=1.3[18] are of the same order of magnitude as the ordering temperatures ($\sim$10K), so that they can be attributed to the interatomic interaction. If the Kondo effect is at all operative in the expanded phase, the T_K should be of order 1$\sim$10K. It is yet to be determined whether it is a low T_K system or one with no Kondo effect.

The resonant photoemission experiment[19] is to date the only direct probe into the 4f state of $CeSi_2$. It is concluded that, in $CeSi_2$, the 4f level is sufficiently deep ($\sim$2eV) below the Fermi level to preclude fractional valence and that it is the rather large ($\sim$0.8eV) 4f width that brings about Kondo behavior with a relatively high T_K ($\sim$200K). If we are to follow their argument, we may interpret the volume transition in $CeSi_{2-x}Ga_x$ as one from a high T_K Kondo system to a magnetically ordering, possibly low T_K system. Our results then seem to be relevant to new theoretical models[20,21], although more experiments are needed before a detailed discussion can be made.

In conclusion, we have observed an alloying-induced discontinuous volume transition in $CeSi_{2-x}Ga_x$ which accompanies a drastic change in its magnetism. The fact that no such transition is seen in $LaSi_{2-x}Ga_x$ indicates that the transition is one closely related to the 4f state of Ce. Finally, we wish to point out an advantage of the present system compared to other systems exhibiting a similar phenomenon.

If Ce is replaced with another rare-earth with a larger radius as in, for instance, $Ce_xLa_{1-x}Pd_3$, the subsequent reduction in T_K necessarily accompanies magnetic dilution. This might render the material incapable of achieving magnetic order even when T_K is sufficiently low. The present method of substituting the non-rare earth seems suitable for studying transitions from a nonmagnetic high T_K state to a magnetically ordering state.

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