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Important role of coherence for the heavy-fermion state in $CeCu_2Si_2$

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The system $Ce(Cu_{1-x}M_x)_{2.2}Si_2$ was doped with M=Pt, Ir, Os, and Ni, always maintaining the original $CeCu_2Si_2$ structure. The doped samples as well as the end points (i.e., $x=1$) are nonmagnetic. Measurements on the specific heat C of lower-doped samples ($x<0.2$) showed a monotonic decrease of γ with increasing doping. This decrease depends *only* on the amount of doping and not on M, thus not on the variation of the lattice constant or the electronic structure of the dopants. We conclude that the decrease in γ is primarily determined by the disturbed coherence in the heavy-fermion lattice, and that variation of the Ce-M ligand hybridization merely plays a secondary role. This result underlines the fact that coherence is a decisive prerequisite for the formation of a heavy-fermion state, and that this coherence is equally dependent on disturbance of the ligand sublattice as of the f-atom sites.

INTRODUCTION

In our attempts to seek the mechanisms leading to the formation of a heavy-fermion state, doping experiments appear to be a suitable way to change continuously substantial parameters of intermetallic compounds. Such experiments revealed, for example, that about 40% of the low-temperature value of γ in UBe_{13} is due to single-ion effects;[1] in UPt_3 it is 50%.[2]

$CeCu_2Si_2$ is a very interesting system for doping experiments, because there are three different sites [f atom (Ce), d atom (Cu), and p atom (Si)], and $CeCu_2Si_2$ was found in 1979 to be a heavy-fermion superconductor by Steglich *et al.*[3] The compound crystallizes in a tetragonal-body-centered structure ($I4/mmm$).[4] There is a superconducting transition at $T_c \approx 0.6$ K and the Sommerfeld parameter γ rises up to 1 J/mole K^2 at lower temperatures.[5] Substitution of Si by Ge leads to an antiferromagnetic state. Jee *et al.*[6] investigated the system $Ce_{1-x}R_xCu_{2.2}Si_2$, where Ce was partially substituted by R= Lu, Y, and La. There was a strong depression of the specific heat and no magnetic transition. The investigation of CeM_2Si_2 brought out different results depending on M. For example, when M= Rh, Pd, Ag, or Au magnetism is observed.[7] For M=Ru γ is 365 mJ/mole K^2 and the system shows metamagnetism.[8] Nonmagnetic systems are achieved when M=Ni, Os, Ir, Pt.[9-11]

In this paper we prepared samples with a partial substitution of copper. By limited doping we hoped to follow the way in which the heavy-fermion ground state evolves in the system $Ce(Cu_{1-x}M_x)_{2.2}Si_2$. Kuentzler *et al.*[9] and Sampathkumaran *et al.*[10] already investigated the system $Ce(Cu_{1-x}Ni_x)_2Si_2$. With increased Ni content the lattice constants decrease and there is a drastic reduction of γ and χ. Since the bond distance is a measure for hybridization they concluded that, based on these data, the tendency for dehybridization of the ligand valence orbitals with the Ce 4f orbital is essential to attain the heavy-fermion ground state.[10]

We wanted to further investigate this thesis by doping with elements that, in contrast to Ni, enlarge the lattice. To minimize possible side issues (e.g., magnetic correlations making determination of γ difficult) we only used metals whose end points $CeM_{2.2}Si_2$ are nonmagnetic, i.e., Ir, Pt, and Os. With this extended set of data we are able to study the influence of the number of d electrons, f-atom-ligand spacing, and the disturbance of homogeneity on the heavy-fermion state.

EXPERIMENT AND RESULTS

Since the $CeCu_2Si_2$ system is known to be very sensitive to copper deficit[12,13] we prepared samples with an excess of 10% on the copper sites $C(Cu_{1-x}M_x)_{2.2}Si_2$. To check for comparability with the measurements from Refs. 9 and 10, we also prepared Ni-doped samples.

The initial elements Ce(Ames), Cu(0.999 995), Pt(0.9995), Ni(0.9999), Ir(0.9995), Os(0.9995), and Si(0.999 999) were arc-melted together under a purified argon atmosphere and remelted six times, because still after the 4th melt there was a visible change in the appearance of the surface of the arc-melted button. The weight loss was less than 0.5%. The samples were annealed for seven days at 850 °C, well below the phase transition point of $CeIr_2Si_2$ at 920 °C($I4/mmm$ below and $P4/nmm$ above).[11] The x-ray powder diffraction was performed in a Siemens D 5000 diffractometer in Bragg-Brentano geometry. We had detected a few peaks of secondary phase which in turn all vanished after the samples had been annealed. As reported by Ishikawa *et al.* the lattice constants of $CeCu_2Si_2$ vary between $a=4.100$, $c=9.891$ and $a=4.113$, $c=9.934$ when the stoichiometry varies within 10% around 1:2:2.[12] The values for our undoped sample were $a=4.102$ (± 0.01) Å and $c=9.915(\pm 0.010)$ Å. Doping with Ir, Pt, and Os raises the lattice parameter (Table I) in contrast to Ni-doped samples, where the lattice shrinks.[10] For $Ce(Cu_{1-x}Os_x)_{2.2}Si_2$ in the region of $0.05<x<0.2$ there was an incipient saturation of the lattice parameters, which remained constant for $x>0.2$. This saturation was used to detect the maximal solubility of Os.

TABLE I. Lattice constants a and c for different Ir, Pt, and Os dopings. The lattice constants for pure $CeCu_{2.2}Si_2$ are $a=4.1021\pm0.001$ Å and $c=9.915\pm0.01$ Å. The maximal solubility for Os (between $x=0.045$ and $x=0.09$) is indicated by the saturation of the lattice constant a.

$Ce(Cu_{1-x}M_x)_{2.2}Si_2$		$x=0.045$	$x=0.09$	$x=0.18$	$x=0.27$
$M=$Ir	$a=$	4.1027	4.1038	4.1064	4.1077
	$c=$	9.918	9.92	9.931	9.935
$M=$Pt	$a=$		4.1091		4.1284
	$c=$		9.927		9.949
$M=$Os	$a=$	4.105	4.1065	4.1079	4.1079
	$c=$	9.918	9.919	9.921	9.921

The maximal solubility of Pt is reached for $Ce(Cu_{0.7}Pt_{0.3})_{2.2}Si_2$.

Ac-susceptibility measurements revealed a superconducting transition temperature of $T_c=630$ mK for the undoped sample. Our available temperature region down to 300 mK was not large enough to investigate the T_c variation with increased doping.

The measurements of susceptibility $\chi(T)$ and magnetization $M(H)$ were performed in a Quantum Design superconducting quantum interference device susceptometer. At 1.8 K all samples (doped or undoped) appear as a Pauli paramagnet up to magnetic fields of 7 T, except for $Ce(Cu_{0.73}Pt_{0.27})_{2.2}Si_2$ where there was a small but visible saturation in $M(H)$. All samples showed Curie-Weiss behavior above $T\approx170$ K with $1/\chi$ vs T plots yielding an effective moment of $\mu_{\text{eff}}\approx2.8\mu_B$.

As already mentioned in Ref. 14 there is a strong sample and orientation dependence of the dc susceptibility χ even in polycrystalline samples. The variation of χ was up to 30% for different orientations in the same sample. Thus the averaged $\chi(T=1.8\text{ K})$ for $Ce(Cu_{1-x}Pt, Ir_x)_{2.2}Si_2$ decreased from 7.5 memu/mole ($x=0$) to about 5 memu/mole ($x=0.18$), but the orientation- and sample-dependent variation foiled any attempt to correlate the variation in χ with the doping rate.

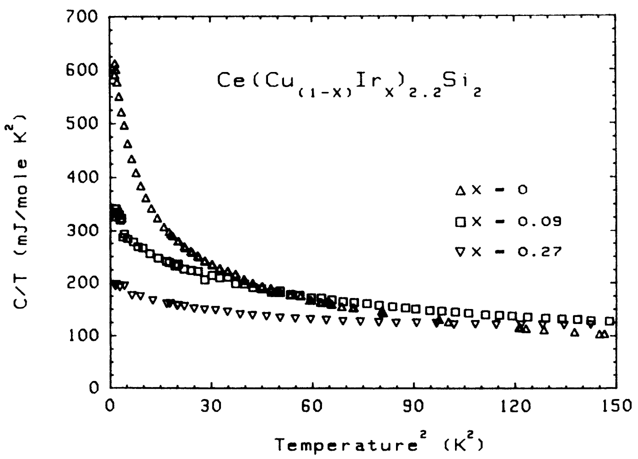

FIG. 1. Specific-heat measurements on $Ce(Cu_{1-x}Ir_x)_{2.2}Si_2$ plotted as C/T vs T^2. The absolute error is 4%, the resolution is 2%.

Much more reliable results are achieved by specific-heat measurements. The specific-heat measurements were performed with a relaxation method,[15,16] with details given in Ref. 17. Our absolute error is ±4% with a resolution of ±2%.

In Fig. 1 are shown specific-heat data $Ce(Cu_{1-x}Ir_x)_{2.2}Si_2$. At the higher temperatures C/T amounts to 100–120 mJ/mole K^2 for all different dopings. Coming to lower temperatures there are different increases that depend on the amount of doped iridium. For Pt- (and Os-doped up to $x=0.045$) doped samples there is nearly the same shape at the same doping rates. With increased doping the parameter $\gamma(C/T$ at 1.25 K) of $Ce(Cu_{1-x}M_x)_{2.2}Si_2$ decreases as shown in Fig. 2 ($M=$ Ni, Pt, Ir, Os). For comparison reasons we have also shown data of $Ce(Cu_{1-x}Ni_x)_2Si_2$ from Ref. 9. We prepared two Ni-doped samples $Ce(Cu_{1-x}Ni_x)_{2.2}Si_2$ on our own and confirmed that the two sets of data are comparable. Figure 2 demonstrates that the decrease of γ (for x up to 0.2) reveals nearly the same rate dependence for the different dopants Pt, Ir, Ni, Os (the maximal solubility of Os warrants data only for $x<0.05$). Any attempt to correlate this decrease with the lattice size or the number of valence electrons completely failed. In particular, it was not possible to see any dependence on the slightly varied lattice parameters a and c. Thus our experiments at low dopings are not in agreement with the thesis[10] that the dehybridization of the ligand valence orbitals with the Ce 4f orbitals is what controls the formation of the heavy-fermion ground state in this system. It seems as if the variation in the lattice size and on the valence electrons is not large enough to provide a sufficient change of hybridization strength. However, there is another important condition for heavy-fermion behavior clearly pointed out by these data. Since the decrease of γ only depends on the doping rate (for $x<0.2$) and not on the lattice size or the number of valence electrons, we conclude that the reduction of γ with increased doping rate is primarily determined by the loss of coherence in the heavy-fermion lattice. In this case, the varia-

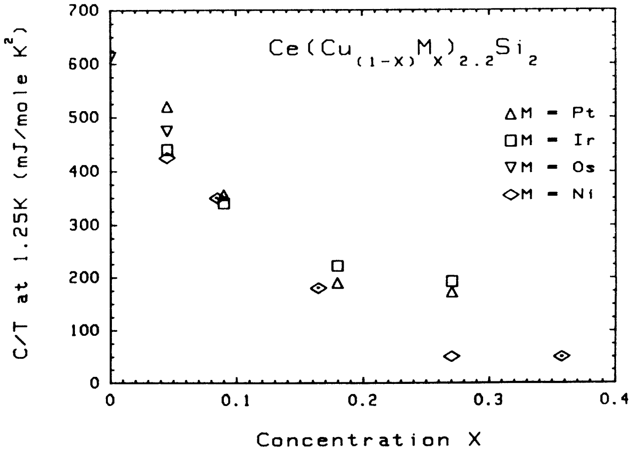

FIG. 2. $\gamma(=C/T$ at $T=1.25$ K) vs doping rate x for $Ce(Cu_{1-x}M_x)_{2.2}Si$, with $M=$Pt, Ir, Os, Ni (this work) and $Ce(Cu_{1-x}Ni_x)_2Si_2$, Ref. 9 (diamonds with the dot). For errors in γ see Fig. 1.

tion of the hybridization strength merely plays a secondary role and becomes important at higher dopings ($x > 0.3$). Thus our experiments indicate that coherence is a decisive prerequisite for the formation of the heavy-fermion state. This is an important feature for such doping experiments, where the influence of other parameters might be masked by coherence effects.

When the heavy-fermion system is described in terms of a coherent Kondo lattice state,[18] the disturbance of coherence means a broadening of the resonance in the electronic density of states. The related decrease in the density of states is then visible in γ. Lawrence, Chen, and Thompson[19] performed comparable investigations on $Ce_{1-x}R_xPd_3$ and found that the resistivity for fixed x was independent of the solute (R = La, Y, Sc). They described the problem by means of a Kondo hole term that exceeds the solute-dependent potential scattering.

Another possible model is given by Aeppli and describes the phenomenon of coherence based on the viewpoint of magnetic correlations.[20] This viewpoint is supported by single-crystal neutron-scattering experiments that revealed strong antiferromagnetic correlations for heavy-fermion systems such as $CeCu_6$, $CeRu_2Si_2$, and UPt_3. When the system is described in terms of antiferromagnetic correlations that are reflected in γ, the disorder reduces the coherence length and thus disrupts these correlations. In this model the weakening of these correlations determines the reduction of γ.

One further comparison may be drawn. Jee *et al.*[6] investigated the system $Ce_{1-x}M_xCu_{2.2}Si_2$ (M= Y, Lu, La). (Since the results for their La-doped samples were suggested to arise from magnetic correlations between the dilute Ce ions, we only consider here the Y- and Lu-doped samples.) The doping dependence of γ for $Ce_{1-x}(Y,Lu)_xCu_{2.2}Si_2$ is almost the same as we observe for $Ce(Cu_{1-x}M_x)_{2.2}Si_2$, with M= Pt, Ir, Os, Ni. Thus, our results show that which is, with hindsight, obvious. The hybridization of the Ce 4f electrons with the neighboring ligand electrons that must take place (since $d_{\text{Ce-Ce}} >$ Hill limit) to form the large m^* observed is symmetrically dependent on disturbances on *either* sublattice, 4f or ligand.

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[1] J. S. Kim, B. Andraka, C. S. Jee, S. B. Ray, and G. R. Stewart, Phys. Rev. B **41**, 11 073 (1990).

[2] G. Fraunberger, M. Baldus, and G. R. Stewart, Phys. Rev. B **47**, 3204 (1993).

[3] F. Steglich, J. Aarts, C. D. Bredl, W. Lieke, D. Meschede, W. Franz, and H. Schäfer, Phys. Rev. Lett. **43**, 1892 (1979).

[4] O. I. Bodak, Ya. M. Kalychak, and E. I. Gladyshevskii, Inorg. Mater. **10**, 388 (1974).

[5] F. Steglich, C. Geibel, S. Horn, U. Ahlhein, M. Lang, G. Sparn, A. Loidl, A. Krimmel, and W. Assmus, J. Magn. Magn. Mater. **90&91**, 383 (1990).

[6] C. S. Jee, B. Andraka, J. S. Kim, and G. R. Stewart, Phys. Rev. B **43**, 2656 (1991).

[7] B. H. Grier, J. M. Lawrence, V. Murgai, and R. D. Parks, Phys. Rev. B **29**, 2664 (1984).

[8] J. D. Thompson, J. O. Willis, C. Godart, D. E. MacLaughlin, and L. C. Gupta, Solid State Commun. **56**, 169 (1985); M. J. Besnus, J. P. Kappler, P. Lehmann, and A. Meyer, Solid State Commun. **55**, 779 (1985).

[9] R. Kuentzler, Y. Dossmann, E. V. Sampathkumaran, S. K. Dhar, and R. Vijayaraghavan, Phys. Rev. B **36**, 788 (1987).

[10] E. V. Sampathkumaran and R. Vijayaraghavan, Phys. Rev. Lett. **56**, 3861 (1986).

[11] K. Hiebl, C. Horvath, and P. Rogl, J. Less-Common Met. **117**, 375 (1986).

[12] M. Ishikawa, H. F. Braun, and J. L. Jorda, Phys. Rev. B **27**, 3092 (1983).

[13] R. Felten, U. Umhofer, U. Rauchschwalbe, and G. Weber, J. Magn. Magn. Mater. **47&48**, 39 (1985); H. Spille, U. Rauchschwalbe, and F. Steglich, Helv. Phys. Acta **56**, 165 (1983).

[14] G. R. Stewart, Rev. Mod. Phys. **56**, 755 (1984).

[15] R. Bachmann, F. J. Di Salvo, Jr., T. H. Geballe, R. L. Greene, R. E. Howard, C. N. King, H. C. Kirsch, K. N. Lee, R. E. Schwall, H.-U. Thomas, and R. B. Zubeck, Rev. Sci. Instrum. **43**, 205 (1972).

[16] G. R. Stewart, Rev. Sci. Instrum. **54**, 1 (1983).

[17] A. Mielke, W. W. Kim, J. J. Rieger, G. Fraunberger, E.-W. Scheidt, and G. R. Stewart (unpublished).

[18] N. Grewe and F. Steglich, *Handbook on the Physics and Chemistry of the Rare Earth,* edited by K. A. Gschneidner and L. Eyring (Elsevier, Amsterdam, 1991), Vol. 14, p. 343.

[19] J. Lawrence, Y.-Y. Chen, and J. Thompson, *Proceedings of the Fifth International Conference on Valence Fluctuations, 5–9 January 1987, Bangalore, India* (Plenum, New York, 1987), p. 169.

[20] G. Aeppli and C. Broholm, in *Handbook on the Physics and Chemistry of the Rare Earth,* edited by K. A. Gschneidner and L. Eyring (Elsevier, Amsterdam, in press), Vol. 19.