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Specific heat of $Ce_{1-x}M_xCu_6$ (M = La, Th, Y, and Pr)

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$Ce_{1-x}La_xCu_6$ is known to have a γ [$\equiv C/T$ $(T \rightarrow 0)$] per Ce mole that *increases* monotonically with increasing La concentration: γ of $Ce_{0.1}La_{0.9}Cu_6$ is ~ 2.3 J/Ce mole K^2 while that for pure $CeCu_6$ is only 1.6 J/Ce mole K^2. To investigate this behavior, unusual in comparison with, e.g., UBe_{13} or $CeCu_2Si_2$, the properties (including specific heat to 0.4 K, dc susceptibility to 1.8 K, and resistivity) of $Ce_{1-x}M_xCu_6$, M = La, Th, Y, and Pr, $0 \leq x \leq 1$, have been investigated, with the most extensive work being on La and Th. χ (1.8 K) remains essentially constant to $x = 0.4$ for Th and La doping, and then rises (falls) for further La (Th) doping, with values for $x = 0.1$ of 45.7 memu/Ce mole for La and 19.3 memu/Ce mole for Th versus 36.7 memu/mole for pure $CeCu_6$. While the specific-heat γ values, as previously reported, increase essentially linearly upon increasing La doping, the γ values for Th doping remain essentially constant up to $x = 0.4$, and then *decrease* monotonically upon further Th doping, reaching $\gamma = 500$ mJ/Ce mole K^2 for $x = 0.9$. This rather abrupt change in the behavior of γ versus Th doping, when compared to published results for specific heat under pressure for pure $CeCu_6$, argues against a simple chemical pressure effect ($ThCu_6$ is smaller than $CeCu_6$). Measurements reported here of the specific heat in field [$C(H)$] of $Ce_{0.6}Th_{0.4}Cu_6$ and $Ce_{0.8}Th_{0.2}Cu_6$, when compared to published $C(H)$ data for $CeCu_6$, $Cu_{0.5}La_{0.5}Cu_6$, and $Ce_{0.1}La_{0.9}Cu_6$, indicate that the large γ value of $CeCu_6$, and its large field dependence, may be due to magnetic correlations and not, in fact, due to a correspondingly enhanced electron effective mass. This interpretation is consistent with known de Haas–van Alphen results and the known nearness to magnetism of $CeCu_6$, where doping [$CeCu_{6-x}(Ag,Au)_x$] produces antiferromagnetism.

INTRODUCTION

Since the discovery[1] of heavy-fermion behavior in $CeCu_6$, a number of interesting properties for this system have been discovered. $CeCu_6$ is certainly a "true" heavy-fermion system, in the sense that the increase in the specific heat divided by temperature, C/T, at low temperatures corresponds to, as proven by de Haas–van Alphen (dHvA) measurements,[2] an increase in the electron effective mass m^*. However, $CeCu_6$ has[3] quite a large response of its low temperature $\gamma(\equiv C/T$ as $T \rightarrow 0)$ to magnetic field (in single-crystal specimens γ is[3,4] depressed by 65% in 7.5 T) in comparison[3] to other heavy-fermion systems, where[5] a large response of C/T to field is a sign that the rise in C/T at lower temperatures is at least partly due to magnetic correlation effects, and not entirely due to the formation of a large m^* ground state. This is consistent with the fact that the dHvA measured[2] m^* values in $CeCu_6$ are approximately a factor of 6 (in Ref. 6, a factor of 3) smaller than expected from the specific-heat data.

The motivation for the present work was another indication that the heavy-fermion ground state of $CeCu_6$ has unusual properties, specifically the measurements of Satoh *et al.*[7] that show that γ of $CeCu_6$, in a per Ce mole basis, rises significantly upon doping with La, e.g., γ (in J/Ce mole K) is 2.3 for $Ce_{0.1}La_{0.9}Cu_6$ vs only 1.6 for pure $CeCu_6$. This slow increase with doping is quite different than what is observed in UBe_{13} (γ falls[8] at least 60% with 90% doping), $CeCu_2Si_2$ (γ initially falls[9] with doping on the Ce site and, in the case of La, rises again—perhaps due[9] to magnetic correlations), or UPt_4Au (where[10] doping with 40% Y on the U site suppresses γ from 700 to 200 mJ/U mole).

EXPERIMENT

We have prepared via arc-melting, $Ce_{1-x}M_xCu_6$, $0 \leq x \leq 1$, for M=La and Th and Y and Pr for $0 \leq x \leq 0.5$. YCu_6 does not form, thus we limited ourselves to 0.5 Y to ensure single-phase material as determined by x-ray diffraction. In the case of Pr, results up to $x = 0.5$ were measured for comparison to Th, which has almost the same lattice parameter. All samples were annealed at 780 °C for one week, and characterized via x-ray powder diffraction. No second phase was detected in the samples reported on here. $CeCu_6$ has a complicated x-ray pattern ($CeCu_6$ has orthorhombic symmetry) and the various $M Cu_6$ samples have rather close reported lattice parameters (for $CeCu_6$, $a = 8.112$ Å, $b = 5.102$ Å, $c = 10.162$ Å; for $LaCu_6$, $a = 8.165$ Å, $b = 5.148$ Å, $c = 10.23$ Å; for $ThCu_6$, $a = 8.115$ Å, $b = 5.078$ Å, $c = 10.122$ Å, for $PrCu_6$, $a = 8.101$ Å, $b = 5.081$ Å, $c = 10.140$ Å, with the respective unit-cell volumes, in Å^3, 420.6, 430.0, 417.1, and 417.4). Thus, $LaCu_6$ is slightly larger than $CeCu_6$, while $ThCu_6$ and $PrCu_6$ are slightly smaller. Our results for $Y_{0.5}Ce_{0.5}Cu_6$ indicate that it is slightly smaller than the corresponding Th compound. Since our ability to determine the lattice parameters precisely is limited by the low relative intensity of the many lines at high-diffraction angle, which are also relatively broad, we are not able to observe $Ce_{1-x}Th_xCu_6$ de-

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creasing in cell volume until $x = 0.4$.

Resistivity, dc susceptibility down to 1.8 K, and specific heat down to 0.4 K were then measured. Measurements as a function of field (magnetization to 5.5 T and specific heat to 14 T) were made with the field perpendicular to the direction determined by the perpendicular to the arc-melter Cu hearth. This is because, as is already known,[2] arc-melt-prepared $CeCu_6$ has a preferential orientation (c axis perpendicular to Cu hearth) and both susceptibility and specific heat have their largest response in the field parallel to a-axis direction. For pure $CeCu_6$, the difference in susceptibility in the chosen direction and perpendicular directions for our annealed samples is around 25%, as was also the case for $Ce_{0.8}Th_{0.2}Cu_6$. This effect is responsible for much of the scatter observed in our field measurements presented below.

RESULTS AND DISCUSSION

Our resistivity results for $Ce_{1-x}La_xCu_6$ are consistent with published results,[11] i.e., the residual resistivity initially rises upon La doping (see Table I), followed by a decrease with further doping, while the maximum in the resistivity shifts to lower temperatures monotonically upon doping, and disappears by 30% La doping. Contrary to this latter behavior, and also contrary to our resistivity data for $Ce_{1-x}Pr_xCu_6$, our data show that the maximum in the resistivity in Th-doped $CeCu_6$ persists up to 40% doping, and is fully suppressed for $x = 0.5$ (see Fig. 1).

Our susceptibility results are summarized in Table I and Fig. 2. As may be seen in Table I and Fig. 2, the low-temperature magnetic susceptibility, within the scatter in our data, remains essentially constant up to 50% Th doping, and then falls rather steeply, while for increasing La doping, a gradual, essentially monotonic increase in χ (1.8 K) is seen. For heavy-fermion systems, e.g., $CeCu_6$, where magnetic correlations do not play a dominant role, the low-temperature susceptibility usually behaves with doping as does the low-temperature specific heat γ. Via the ratio (the so-called Wilson ratio) of $\chi\ (T \rightarrow 0)/\gamma$, where γ is defined as $C/T\ (T \rightarrow 0)$, one can follow the relative strength of magnetic correlations in a given doped system, since an increase in this ratio indicates strengthening of such correlations. Thus, prior to our discussion of our specific-heat data, it is worthwhile to stress that the behavior of χ (1.8 K) vs Th doping (and, to a lesser extent, the continued existence of a peak in ρ vs T for Th-doped $CeCu_6$ past where La doping has already achieved full suppression) seems to point to a rather sudden change in behavior of either the magnetic correlations or the electron effective mass m^* in $Ce_{1-x}Th_xCu_6$ around $x = 0.5$. Such a transition is very unlike the behavior seen in $Ce_{1-x}La_xCu_6$ or, for that matter, in any other doped heavy-fermion system[8–10] of which we are aware.

Another indicator of the strength of magnetic correlations (or, formulated in another way, the "nearness" to magnetism) in a heavy-fermion system is the response of the magnetization to an applied field. The small saturation in M vs H seen in pure $CeCu_6$ (M extrapolated to 5.5 T from our lower field data is 5% larger than what is measured) does not appear to vary with either La, Th, or (up to $x = 0.5$) Pr, and Y doping. Thus, based on our resistivity, χ (1.8 K) and M vs H results for $Ce_{1-x}M_xCu_6$, $M = La$ and Th, the apparent transition for Th doping seen in Fig. 2 appears consistent with primarily an effective-mass effect, i.e., something that would appear in the low-temperature specific heat γ.

Our zero-field specific heat results down to 0.4 K for $Ce_{1-x}M_xCu_6$, $M = La$, Th, Y, and Pr, and the published result[12] for $Ce_{0.1}Pr_{0.9}Cu_6$ are presented in Table I and Figs. 3 and 4. As was already known, γ per Ce mole rises with increase in La doping. We have also included in Fig. 3, the data of Satoh *et al.*[7] for $Ce_{1-x}La_xCu_6$ for our lowest temperature of measurement, 0.4 K. Although

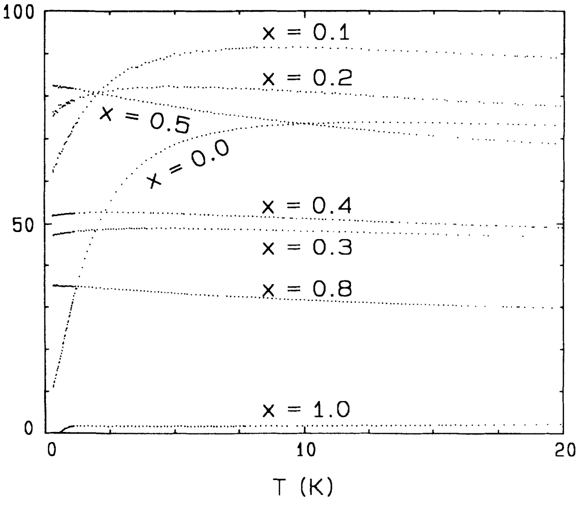

FIG. 1. Resistivity vs temperature for $Ce_{1-x}Th_xCu_6$. Note that there is still a peak in R vs T for $x = 0.4$.

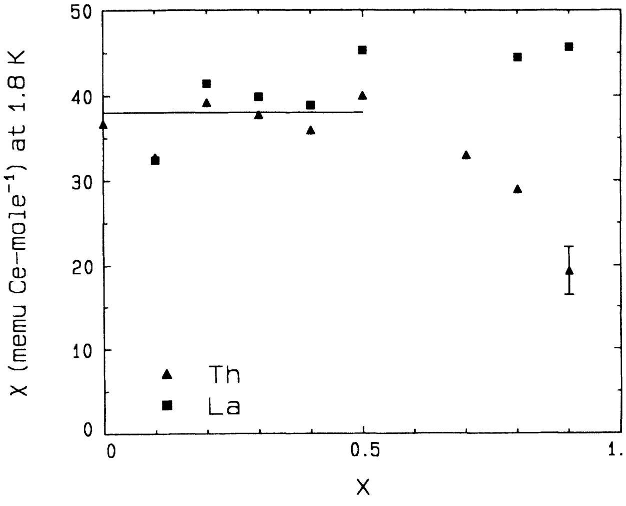

FIG. 2. Low-temperature ($T = 1.8$ K) magnetic susceptibility, per Ce mole, of $Ce_{1-x}M_xCu_6$, $M = Th$ and La. The line shows $\chi = 38$ memu and is a guide to the eye.

TABLE I. Measured parameters of $Ce_{1-x}M_xCu_6$.

	C/T(0.4 K) (mJ/Ce mole K^2)	χ(1.8 K) memu/Ce mole	χ(1.8 K)/C/T(0.4 K)	ρ(1 K) ($\mu\Omega$ cm)
$CeCu_6$	1340	36.7	0.0274	11
	La/Th/Y/Pr	La/Th/Y/Pr	La/Th/Y/Pr	La/Th/Y/Pr
$Ce_{0.9}M_{0.1}Cu_6$	1340/1250/1260/...	32.4/32.8/29.2/30.5	0.0242/0.0262/0.0232/...	69/62/72/...
$Ce_{0.8}M_{0.2}Cu_6$	1400/1300/.../1300	41.4/39.2/26.9/27.2	0.0296/0.0302/.../0.0209	90/77/.../61
$Ce_{0.7}M_{0.3}Cu_6$	1420/1115/1030/...	39.9/37.7/27.0/23.9	0.0281/0.0338/0.0262/...	79/48/.../...
$Ce_{0.6}M_{0.4}Cu_6$	1420/1315/.../1150	38.9/35.9/29.2/25.4	0.0274/0.0273/.../0.0221	93/52/.../72
$Ce_{0.5}M_{0.5}Cu_6$	1520/1200/980/1090	45.3/40.0/25.0/22.7	0.0298/0.0333/0.0255/0.0208	93/82/.../87
$Ce_{0.3}M_{0.7}Cu_6$	.../810/.../...	.../33.0/.../...	.../0.0407/.../...	.../.../.../...
$Ce_{0.2}M_{0.8}Cu_6$	1675/800/.../...	44.5/29.0/.../...	0.0266/0.0362/.../...	54/35/.../...
$Ce_{0.1}M_{0.9}Cu_6$	1710/505/.../890	45.7/19.3/.../...	0.0267/0.0382/.../...	.../.../.../...

the disagreement between our data and theirs exceeds the summed limits of error, the trend clearly remains the same.

What we wish to focus on, however, for the rest of this paper is the anomalous behavior, and the cause, therefore, of γ for $Ce_{1-x}Th_xCu_6$ as seen in Table I and Figs. 3 and 4. Just as is seen clearly in the χ (1.8 K) data in Fig. 2, there is a rather abrupt change in γ vs Th doping around $Ce_{0.5}Th_{0.5}Cu_6$. The 60% decrease this makes in the low-temperature specific-heat per Ce mole is graphically displayed in Fig. 4. This decrease is the same size or larger than the increase in γ per Ce mole in $Ce_{0.1}La_{0.9}Cu_6$ compared to pure $CeCu_6$ observed[7] by Satoh *et al.* What is different for Th (see Table I and Figs. 3 and 4) is that no change is seen in γ (or low temperature χ) up to 50% doping, whereas for La, the change is essentially linear in doping (see Fig. 3).

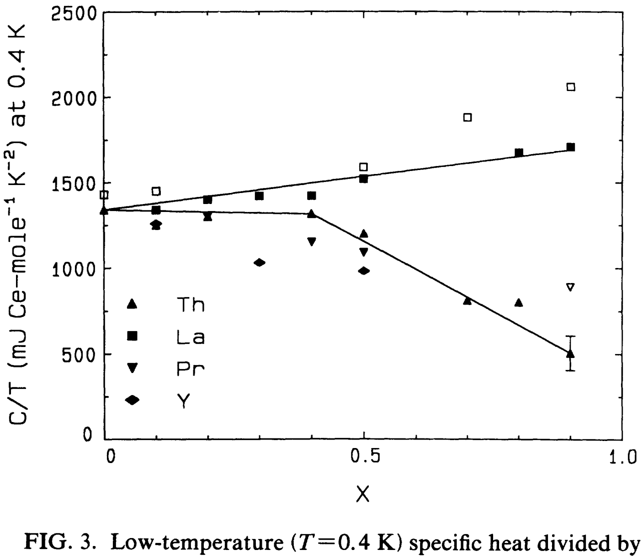

FIG. 3. Low-temperature (T=0.4 K) specific heat divided by temperature data vs doping in $Ce_{1-x}M_xCu_6$. The open squares are M=La data from Ref. 7. The open inverted triangle is for M=Pr data from Ref. 12. $PrCu_6$ itself has a χ (1.8 K) = 72 memu/mole, indicative of magnetic correlations. Thus, although $ThCu_6$ and $PrCu_6$ are essentially equally "compressed" from $CeCu_6$, the quite strong magnetic correlations presented in pure $PrCu_6$ vs $ThCu_6$ [χ (1.8 K) for $ThCu_6$ equals 0.15 memu] may explain why the γ for $Ce_{0.1}Pr_{0.9}Cu_6$ is not as suppressed as that for $Ce_{1-x}Th_xCu_6$.

Fortunately for our current discussion, specific-heat data under pressure exist[4] for $CeCu_6$. Based on the known[13] Grüneisen parameter, the highest pressure used[4] in the measurement (8.8 kbar) is equivalent to a decrease in the $CeCu_6$ lattice volume of 0.97%, while pure $ThCu_6$ has a lattice volume 0.83% smaller than pure $CeCu_6$. Thus, the two sets of data γ vs physical (Ref. 4) and "chemical" pressure, i.e., our doping via Th data) may be intercompared to separate out atomic separation effects from "coherence" effects. The latter refers to effects seen in the electronic properties of heavy-fermion systems where the primary difference is that physical pressure does not interrupt the 100% occupancy of the f-atom sublattice. Thus, it has been shown[8] that 40% of the large γ observed in pure UBe_{13} is due to a coherence effect (i.e., all of the U sites are occupied with U), while the rest of the γ is a single-ion effect, independent of the fractional occupancy of the U sublattice.

What the specific heat under pressure data for $CeCu_6$ show[4] is a monotonic decrease in γ with increasing pressure, specifically −17.4% (2 kbar), −30.5% (4.1 kbar),

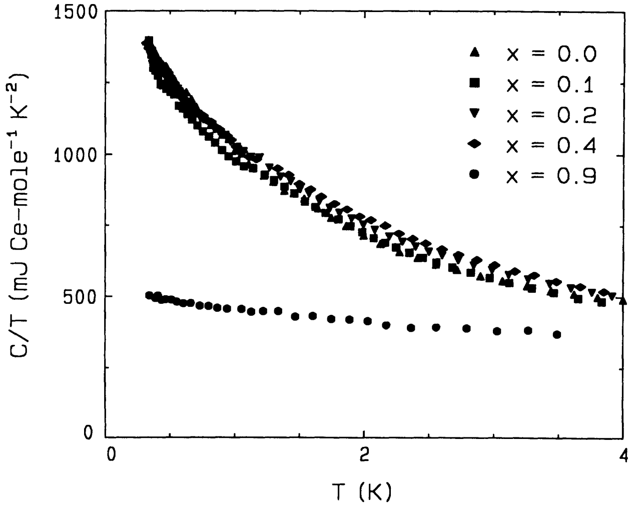

FIG. 4. Specific heat per Ce mole divided by temperature vs temperature for $Ce_{1-x}Th_xCu_6$. These data show quite clearly the difference in behavior for Th doping for $x > 0.4$.

and -51% (8.8 kbar). Thus, the data presented herein for Th-doped $CeCu_6$ display two differences to the pressure results. First, obviously, little or no change in γ is observed up to $Ce_{0.5}Th_{0.5}Cu_6$. If one assumes that Th doping causes a monotonic decrease in lattice volume (as mentioned earlier, difficulty in determining lattice parameters accurately and the small changes involved make it difficult to see a fall in unit-cell volume until 40% Th doping), then an explanation based on coherence effects must be found to explain that the γ for $Ce_{0.6}Th_{0.4}Cu_6$ (where the lattice parameter, based on a linear extrapolation, is equivalent to 3 kbar) remains unchanged while the equivlant under pressure measurement would show a -20% change in γ. That the changes in γ and χ observed here for $Ce_{1-x}Th_xCu_6$, $x>0.5$, are, indeed, primarily a size effect, and not due to the electronic nature of Th vs La, can be checked by measurements on $Ce_{0.1}La_{0.9-x}Th_xCu_6$ where x may be chosen to give the lattice parameter of pure $CeCu_6$. We have prepared $Ce_{0.1}La_{0.356}Th_{0.544}Cu_6$ [$(0.356\times$cell volume $LaCu_6+0.544\times$cell volume $ThCu_6)/0.9$ gives 422 Å vs 420.6 for pure $CeCu_6$] and find $C/T\,(0.4\text{ K})=1400$ mJ/ce mole K^2 and χ (1.8 K) = 43 memu/Ce mole. This result (compare Table I) supports the supposition that size is the more determining factor for the larger dopings.

The second question raised by the Th-doped $CeCu_6$ data is, what changes around 50% Th to cause the sudden decrease in γ and χ (1.8 K) with increasing doping? Of course, any unifying explanation must also explain why Th behaves so differently than La, particularly for explanations involving coherence.

As a further method of investigating these results, it occurred to us that, since pure[3] $CeCu_6$ and $Ce_{1-x}La_xCu_6$ (Ref. 7) both show a large dependence of γ on applied field, one should measure as well $Ce_{0.6}Th_{0.4}Cu_6$ and $Ce_{0.2}Th_{0.8}Cu_6$ in field to determine if this "transition" versus Th doping also affects the field response. Our specific-heat results in fields to 14 T are shown in Fig. 5. Although the published data[7] for C(H) of $Ce_{1-x}La_xCu_6$ only extend to 5 T, it is clear that field depresses γ for $CeCu_6$ and $Ce_{1-x}La_xCu_6$ essentially equally strongly, while already for 40% Th doping, the field response is decreased by a factor of 2, while for 80% Th doping, the field response is a factor of 5 reduced.

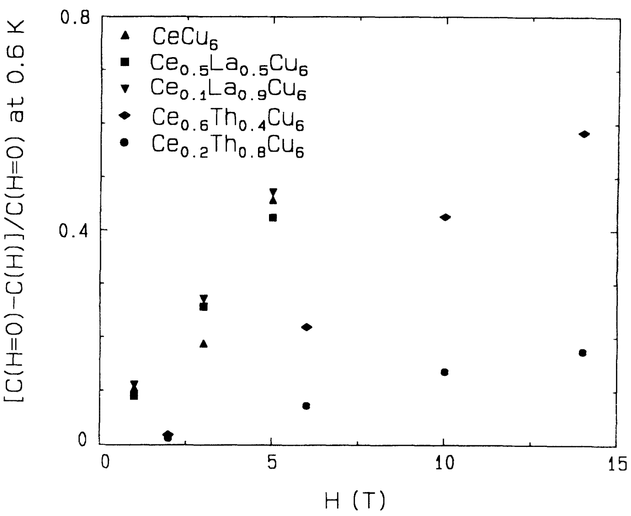

FIG. 5. Fractional change of the low-temperature ($T=0.6$ K) specific heat vs field for $CeCu_6$ (Ref. 7), $Ce_{0.5}La_{0.5}Cu_{0.6}$ (Ref. 7), $Ce_{0.1}La_{0.9}Cu_6$ (Ref. 7), $Ce_{0.6}Th_{0.4}Cu_6$, and $Ce_{0.2}Th_{0.8}Cu_6$. Note that increasing Th doping significantly decreases the change with magnetic field of the low-temperature specific heat.

CONCLUSION

Whatever causes the changes in the Ce f electron-created γ in $Ce_{1-x}Th_xCu_6$ for $x>0.5$, the ground state that exists for $x>0.5$ resembles more closely UBe_{13} or superconducting $CeCu_2Si_2$ in its response of γ to field than pure $CeCu_6$ or $Ce_{1-x}La_xCu_6$. A unifying explanation of all of these data, consistent with the dHvA data, is that a significant fraction of the observed γ in pure $CeCu_6$ comes from magnetic correlations and that these correlations (and the corresponding γ and field dependence thereof) are suppressed when the lattice is compressed. (A recent theory,[14] in fact, attempts to explain the heavy-fermion ground state in general, as primarily caused by magnetic correlations.) It remains, of course, unexplained why the Th γ and χ data show such a sharp change around $x=0.5$. More precise lattice-parameter determinations, preferably below the known phase transition at 200 K, on $Ce_{1-x}Th_xCu_6$ are needed.

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[1] G. R. Stewart, Z. Fisk, and M. S. Wire, Phys. Rev. B **30**, 482 (1984).

[2] P. H. P. Reinders, M. Springford, P. T. Coleridge, R. Boulet, and D. Ravot, Phys. Rev. Lett. **57**, 1631 (1986).

[3] B. Andraka, G. Fraunberger, J. S. Kim, C. Quitmann, and G. R. Stewart, Phys. Rev. B **39**, 6420 (1989); A. S. Edelstein, B. N. Das, W. W. Fuller, B. Andraka, and G. R. Stewart, Physica B **163**, 504 (1990).

[4] R. A. Fisher, S. E. Lacy, C. Marcenat, J. A. Olsen, N. E. Phillips, J. Flouquet, A. Amato, and D. Jaccard, Jpn. J. Appl. Phys. **26**, Suppl. 26-3, 1257 (1987).

[5] B. Andraka, J. S. Kim, G. R. Stewart, and Z. Fisk, Phys. Rev. B **44**, 4371 (1991).

[6] S. Chapman, M. Hunt, P. Meeson, P. H. P. Reinders, M. Springford, and M. Norman, J. Phys. Condens. Matter **2**, 8123 (1990). In this reference, account is taken of the field dependence of the dHvA measured masses.

[7] K. Satoh, M. Kato, Y. Maeno, T. Fujita, Y. Onuki, and T. Komatsubara, Jpn. J. Appl. Phys. **26**, Suppl. 26-3, 521 (1987); K. Satoh, T. Fujita, Y. Maeno, Y. Onuki, and T. Komatsubara, J. Phys. Soc. Jpn. **58**, 1012 (1989).

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

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

[10] S. G. Thomas, W. W. Kim, J. S. Kim, B. Andraka, and G. R. Stewart (unpublished).

[11] Y. Onuki, Y. Shimizu, M. Nishihara, Y. Machii, and T. Komatsubara, J. Phys. Soc. Jpn. **54**, 1964 (1985).

[12] S. B. Roy, G. R. Stewart, and B. R. Coles, J. Magn. Magn. Mater. **97**, 291 (1991).

[13] A. Shibata, G. Oomi, Y. Onuki, and T. Komatsubara, J. Phys. Soc. Jpn. **55**, 2086 (1986).

[14] Yu. Kagan, K. A. Kikoin, and N. V. Prokog'ev, Physica B **182**, 201 (1992).