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### Title

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### Journal

Journal of the Less Common Metals, 124(1-2)

### ISSN

0022-5088

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### Publication Date

1986-10-01

### DOI

10.1016/0022-5088(86)90496-0

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## LOW-TEMPERATURE PROPERTIES OF $U_{1-x}Th_xRe_2$

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(Received April 17, 1986)

### Summary

The high-temperature structural phase transition in  $URE_2$  is only moderately influenced by thorium impurities at low concentrations but disappears rapidly when the thorium content exceeds 25%. Replacing thorium in  $ThRe_2$  by uranium reduces its critical temperature for the onset of superconductivity but much less drastically than do uranium impurities in metallic thorium. A comparison of the low-temperature specific heats of  $URE_2$  and  $ThRe_2$  indicates that the density of f-electron states at the Fermi energy  $E_F$  in  $URE_2$  is not large and that the f electrons in  $URE_2$  behave similarly to d electrons in non-magnetic d transition metals.

### 1. Introduction

The recent discovery of various exciting low-temperature properties of uranium intermetallics has led to considerable general interest in the behaviour of metallic uranium compounds.  $UBe_{13}$  [1] and  $UPt_3$  [2] have been found to be superconductors below 1 K involving electrons with very large effective masses in forming the superconducting state. Various experiments indicate that this superconducting state is characterized by unconventional pairing of the electrons [3 - 6].  $U_2Zn_{17}$  [7] and  $UCd_{11}$  [8] order magnetically, preserving a very large electronic specific heat below the phase-transition temperature. These four compounds all have in common the fact that the separation of the uranium atoms in the crystal lattice exceeds 4 Å. In all cases the low-temperature specific heat is dominated by a term varying linearly with temperature ( $c_p \approx \gamma T$ ) and which is ascribed to large densities of electronic states  $N(E_F)$  at the Fermi energy.

There is no simple relationship between the U-U separation and the type of phase transition that occurs at low temperatures. This separation only slightly exceeds 4 Å for  $UPt_3$  [9] and  $U_2Zn_{17}$  [10] but is more than 5 Å

for  $\text{UBe}_{13}$  [11] and more than 6 Å for  $\text{UCd}_{11}$  [12]. However, when comparing the  $c_p/T$  values per formula unit and per mole as a measure of the electronic specific heat just above the respective transition temperatures it is evident that these ratios are considerably larger for  $\text{UBe}_{13}$  [1] and  $\text{UCd}_{11}$  [8] than for  $\text{UPt}_3$  [2] and  $\text{U}_2\text{Zn}_{17}$  [7].

With respect to phase transitions, uranium-based materials with U–U distances much smaller than 4 Å are also of interest. A well-known example is elemental uranium with different stable crystal structures depending on temperature [13].  $\text{URe}_2$  is another substance with a structural phase transition, transforming from a hexagonal high-temperature phase to an orthorhombic phase that is stable at low temperatures [14]. This transition is almost certainly connected with the 5f electrons of the uranium atoms because  $\text{ThRe}_2$  remains hexagonal at all temperatures below the melting point and therefore further studies of  $\text{URe}_2$  seemed of interest. We report here the results of various measurements on the (U,Th) $\text{Re}_2$  system including room-temperature lattice parameters, specific heat, magnetic susceptibility and electrical resistivity. We investigated especially how replacement of uranium by thorium in  $\text{URe}_2$  influences the above mentioned structural phase transition and also how uranium impurities influence the superconductivity of  $\text{ThRe}_2$ .

$\text{ThRe}_2$  and the high-temperature modification of  $\text{URe}_2$  crystallize in the hexagonal  $\text{MgZn}_2$ -type structure [15]. The room-temperature modification of  $\text{URe}_2$ , however, is an orthorhombically distorted version of the hexagonal C14 structure [14]. The published data on the variation of the  $\text{URe}_2$  cell with temperature suggest a first-order transition, albeit with small discontinuities of the lattice parameters. As Hatt [14] pointed out, the curves for the near-neighbour distances intersect near 1000 °C when all U–U distances are equal to 3.29 Å, Re–Re is 2.69 Å and U–Re is 3.15 Å. At this temperature the C14 Laves phase structure would have the ideal axial ratio  $(8/3)^{1/2}$ . At helium temperatures the U–U distances in the distorted structure lie between 3.1 and 3.4 Å so that it may be expected that the uranium 5f electrons in  $\text{URe}_2$  form a band of electronic states by direct overlap of the wavefunctions at all temperatures.

## 2. Experimental details and results

First we studied the  $\text{U}_{1-x}\text{Th}_x\text{Re}_2$  system by determining the room-temperature lattice constants and the transition temperatures. All samples were prepared by melting the components or certain master alloys in an argon arc furnace with a water-cooled copper hearth. All compositions showed congruent-melting behaviour. The quality of the samples was judged from Guinier photographs taken with copper radiation. The lattice constants (see Table 1) were derived with silicon ( $a_{295\text{K}} = 5.43047$  Å) as an internal standard. The orthorhombic-to-hexagonal transition was studied on powder samples of 80 to 250 mg using an automatic differential thermal analysis

TABLE 1

Room-temperature data for lattice constants, unit-cell volumes and orthorhombic deformations of  $URe_2$ ,  $(U,Th)Re_2$ ,  $ThRe_2$  and (for comparison)  $(U,Y)Re_2$

Parameter	$URe_2(44)^a$	$URe_2(82)^a$	$U_{0.98}Th_{0.02}Re_2$	$U_{0.95}Th_{0.05}Re_2$	$U_{0.9}Th_{0.1}Re_2$	$U_{0.82}Th_{0.18}Re_2$	$U_{0.75}Th_{0.25}Re_2$	$U_{0.9}Y_{0.1}Re_2$	$U_{0.7}Th_{0.3}Re_2$
$a$ (Å)	5.5932(5)	5.5943(4)	5.6038(4)	5.5968(5)	5.5770(6)	5.5453(5)	5.4847(5)	5.5560(5)	5.3988(5)
$b$ (Å)	9.1828(13)	9.1772(6)	9.1668(9)	9.1650(8)	9.1631(9)	9.1818(8)	9.2333(8)	9.2017(9)	9.3510(8)
$c$ (Å)	8.4746(9)	8.4727(6)	8.4928(6)	8.5264(7)	8.5852(8)	8.7030(8)	8.8029(6)	8.5283(8)	8.8916(14)
$V$ (Å <sup>3</sup> )	435.3	435.0	436.3	437.4	439.4	443.1	445.8	436.0	448.9
$1 - \frac{b}{a} \frac{3^{1/2}}{2}$	0.0521	0.0529	0.0556	0.0546	0.0509	0.0440	0.0281	0.0438	

	$U_{0.65}Th_{0.35}Re_2$	$U_{0.5}Th_{0.5}Re_2$	$U_{0.25}Th_{0.75}Re_2$	$U_{0.18}Th_{0.82}Re_2$	$U_{0.1}Th_{0.9}Re_2$	$U_{0.05}Th_{0.95}Re_2$	$U_{0.03}Th_{0.97}Re_2$	$U_{0.01}Th_{0.99}Re_2$	$ThRe_2$
$a$ (Å)	5.4004(6)	5.4193(3)	5.4542(4)	5.4653(4)	5.4748(5)	5.4836(2)	5.4885(3)	5.4891(4)	5.4930(4)
$a3^{1/2}$ (Å)	9.3538(9)	9.3864(5)	9.4469(7)	9.4661(8)	9.4826(9)	9.4978(4)	9.5063(5)	9.5075(7)	9.5142(7)
$c$ (Å)	8.922(2)	8.9716(8)	9.0296(10)	9.0556(9)	9.0662(12)	9.0789(5)	9.0886(6)	9.0935(9)	9.1019(8)
$V$ (Å <sup>3</sup> )	450.7	456.4	465.5	468.5	470.7	472.9	474.2	474.6	475.7

<sup>a</sup>44 and 82 denote 2 different batches.

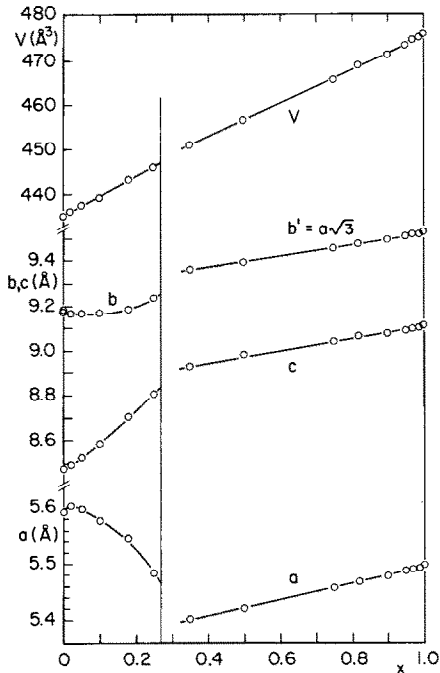


Fig. 1. Room-temperature lattice constants and unit-cell volumes for  $U_{1-x}Th_xRe_2$  as a function of  $x$ .

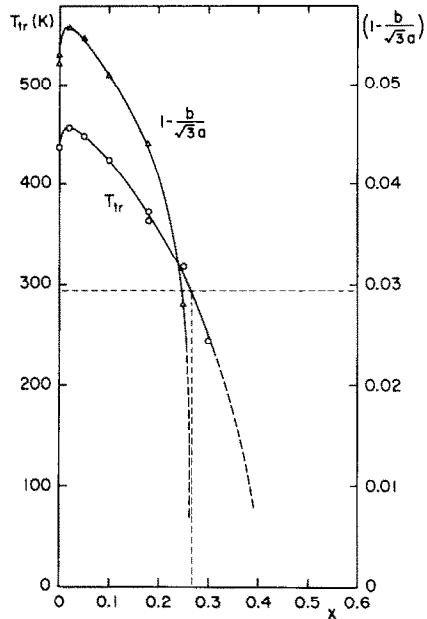


Fig. 2. Transition temperatures  $T_{tr}$  and room-temperature orthorhombic deformations for the structural phase transition of  $U_{1-x}Th_xRe_2$  as a function of  $x$ .

(DTA) apparatus between 200 and 500 K with scan rates of about 20 K  $\text{min}^{-1}$ .

The results of these measurements are summarized in Table 1 and Figs. 1 and 2. Figure 1 shows the variation of the room-temperature lattice parameters and the unit-cell volume with the concentration  $x$ . In Fig. 2 we show the  $x$  dependence of the transformation temperature as determined from DTA and of the orthorhombic deformation in the form  $(1 - b/(3^{1/2}a))$ . Table 1 contains the same information in tabulated form. From the DTA measurements (see Fig. 2) we expect that the transformation temperature for  $U_{1-x}Th_xRe_2$  falls to below room temperature for  $x = 0.27$ . The concentration dependence of the room-temperature lattice parameters (see Fig. 1) then suggests that this transformation is discontinuous with only a very small volume change. It is remarkable that the highest transformation temperature and the strongest distortion does not occur in pure  $URe_2$  but close to  $x = 0.02$ . The estimated enthalpies of the transformation are 100  $\text{J mol}^{-1}$  for  $URe_2$  and 190, 210, 150, 130 and 60  $\text{J mol}^{-1}$  for  $x = 0.02, 0.05, 0.1, 0.18$  and  $0.25$  respectively.

Previous reports on low-temperature properties of  $URe_2$  and  $ThRe_2$  include measurements of the magnetic susceptibility between 2 and 300 K [16], revealing almost temperature-independent susceptibilities  $\chi$  of the

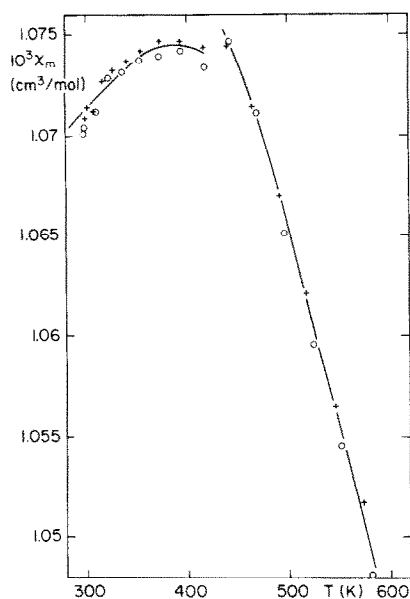


Fig. 3. Temperature dependence of the magnetic susceptibility of  $\text{URe}_2$  between 280 and 600 K. Crosses denote data taken with increasing temperature, open circles with decreasing temperature.

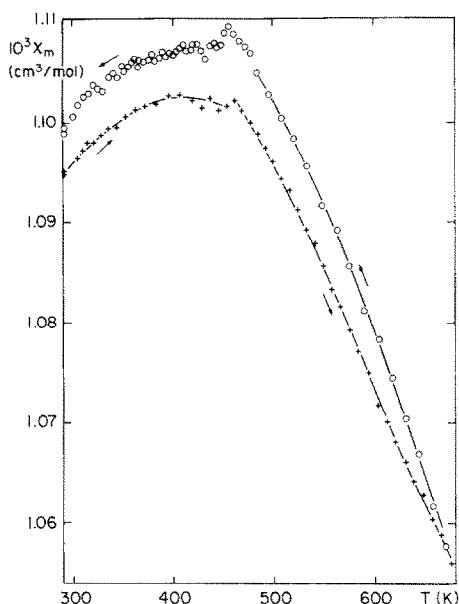


Fig. 4. Temperature dependence of the magnetic susceptibility of  $\text{U}_{0.95}\text{Th}_{0.05}\text{Re}_2$  between 280 and 700 K.

order of  $10^{-3} \text{ cm}^3 \text{ mol}^{-1}$ . We repeated these measurements and extended them to temperatures of about 700 K. Below room temperature  $\chi$  was measured with a moving-sample magnetometer and above 300 K a Faraday balance was used. The magnetic behaviour of  $\text{U}_{1-x}\text{Th}_x\text{Re}_2$  with varying  $x$  is very similar to that of pure  $\text{URe}_2$  for  $x < 0.1$ . Above 2 K,  $\chi$  increases weakly with increasing temperature and saturates near 400 K. After a tiny discontinuity it decreases almost linearly with further increase in temperature, as may be seen in Fig. 3 for  $\text{URe}_2$ . Figure 4 shows similar data for  $\text{U}_{0.95}\text{Th}_{0.05}\text{Re}_2$ . In both cases we show only the data obtained above room temperature, since at lower temperatures we confirm the results of Brodsky *et al.* [16]. The small discontinuities in  $\chi(T)$  between 400 and 500 K occur at the same temperatures that the respective DTA scans indicate phase transitions. The small hysteresis that is observed for  $\chi(T)$  of  $\text{U}_{0.95}\text{Th}_{0.05}\text{Re}_2$  should be noted. The slight difference in the transition temperatures of the heating cycle and the cooling cycle is also observed in the DTA measurements.

In Fig. 5 we show the low-temperature electrical resistivity  $\rho$  of  $\text{URe}_2$  between 2 and 300 K, with the same general features as those observed in other uranium materials (see, for example, ref. 17). Below 10 K,  $\rho(T)$  appears to vary as  $T^2$  but distinct deviations from this behaviour below 3 K make it doubtful that this observed temperature dependence of  $\rho$  has any

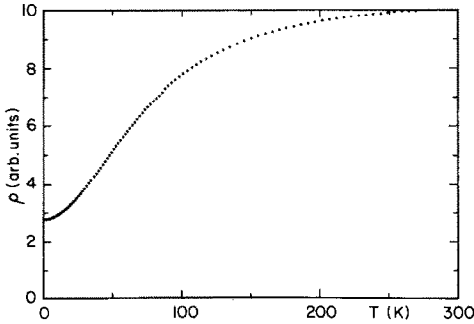


Fig. 5. Temperature dependence of the electrical resistivity of  $\text{URe}_2$  between 1.5 and 300 K. The room-temperature resistivity is of the order of a few times  $10 \mu\Omega \text{ cm}$ .

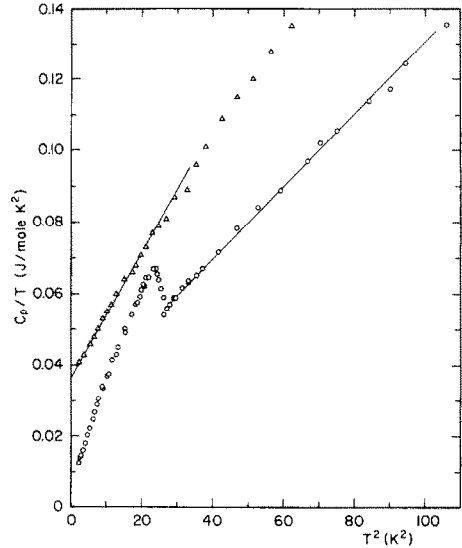


Fig. 6. Comparison of  $c_p/T$  vs.  $T^2$  for  $\Delta$ ,  $\text{URe}_2$  and  $\circ$ ,  $\text{ThRe}_2$  between 1.5 and 10 K.

significance in connection with the often quoted Fermi-liquid behaviour in similar compounds (see, for example, ref. 18).

$\text{ThRe}_2$  was previously reported to be a superconductor below 5 K [19]. Our measurement of the low-temperature specific heat confirms this and the data are shown in Fig. 6. The magnitude of the discontinuity  $\Delta c_p$  at the transition and also the behaviour for  $T \ll T_c$  may be taken as an indication that the entire bulk of the sample does not reach the superconducting state. As may be seen from Fig. 6, the data above 5 K can be represented fairly well by

$$c_p = \gamma T + \beta T^3 \quad (1)$$

where  $\gamma = 28.5 \pm 1 \text{ mJ mol}^{-1} \text{ K}^{-2}$  and  $\beta = 1.0 \text{ mJ mol}^{-1} \text{ K}^{-4}$ . It is now quite interesting to compare the low-temperature specific heat of  $\text{ThRe}_2$  with that of  $\text{URe}_2$ , also shown in Fig. 6. Below 5 K, the data for  $\text{URe}_2$  can also be represented by eqn. (1) and the resulting parameters are  $\gamma = 36.5 \pm 1 \text{ mJ mol}^{-1} \text{ K}^{-2}$  and  $\beta = 1.77 \text{ mJ mol}^{-1} \text{ K}^{-4}$ . This  $\gamma$  value for  $\text{URe}_2$  is close to that reported previously by Brodsky *et al.* [16].

### 3. Discussion

What is surprising is the relatively large low-temperature electronic specific heat of  $\text{ThRe}_2$  in its normal state. An electronic specific-heat parameter  $\gamma$  of  $28.5 \text{ mJ mol}^{-1} \text{ K}^{-2}$  for  $\text{ThRe}_2$  is not much less than  $\gamma = 36.5 \text{ mJ}$

$\text{mol}^{-1} \text{K}^{-2}$  for  $\text{URe}_2$ , indicating a rather large density of d-electron states at the Fermi energy  $E_F$ . This may in fact be due to a favourable electron band structure because, for both compounds  $\gamma$  is considerably larger than for the elements thorium [20] and uranium [21]. The fact that  $\gamma$  for  $\text{URe}_2$  is not more enhanced, above that of  $\text{ThRe}_2$ , may possibly be traced back to the different crystal structures of the two compounds at low temperatures. It is quite likely that the high-temperature structural phase transition induces gaps in the electronic excitation spectrum of  $\text{URe}_2$ .

As we mentioned in the Introduction it seems reasonable to assume that the low-temperature thermal properties of  $\text{URe}_2$  are dominated by the formation of a narrow band of electronic states. This also seems more or less to be confirmed by the temperature-independent magnetic susceptibility of about  $10^{-3} \text{ cm}^3 \text{ mol}^{-1}$ , a likely value for a Pauli susceptibility of a narrow band. If we compare the low-temperature values of  $\chi$  and  $\gamma$  of  $\text{URe}_2$  in the usual way by forming the ratio  $k_B^2 \pi^2 \chi / 3 \mu_B^2 \gamma$ , we obtain a value of 2.0. It is therefore reasonable to assume that both  $\chi$  and  $\gamma$  are due to a fairly large density of states of itinerant d and f electrons at  $E_F$ . It is very likely, however, that  $\gamma$  and also  $\chi$  would be larger if the structural transition were absent. This we conjecture qualitatively from the temperature dependence of  $\chi$  shown in Fig. 3. The phase transition obviously reduces the magnetic susceptibility and this we ascribe to a reduction of f-electron density of states at  $E_F$ .

Unfortunately our data give no real clue with regard to the driving mechanism of the phase transition in  $\text{URe}_2$ . The most likely cause might be the formation of a charge-density-wave state but it is then surprising that replacing uranium by thorium initially enhances the transition temperature. From the low-temperature specific-heat experiments we notice a sizeably lower Debye temperature for  $\text{URe}_2$  than for  $\text{ThRe}_2$ . From the  $T^3$  contributions to  $c_p$  we calculate values for  $\theta_D(0)$  of 149 K and 180 K for  $\text{URe}_2$  and  $\text{ThRe}_2$ , respectively, indicating the softening influence of the 5f electrons on the crystal lattice of  $\text{URe}_2$  even in the distorted phase. The decreasing slope of the  $c_p/T$  versus  $T^2$  plot of  $\text{URe}_2$  above 5 K (see Fig. 6) is comparable with that observed for other uranium compounds with similar behaviour of the low-temperature magnetic susceptibility and specific heat, such as  $\text{U}_6\text{Fe}$  [22] or uranium compounds with  $\text{Cu}_3\text{Au}$  structure [23].

With regard to possible interactions in the (Th,U) $\text{Re}_2$  system it is of interest to note that the depression of the superconducting transition temperature  $T_c$  of  $\text{ThRe}_2$  when replacing thorium with uranium is far less drastic than that for elemental thorium when adding uranium. In Fig. 7 we show a comparison of these two cases. The data for  $\text{Th}_{1-x}\text{U}_x\text{Re}_2$  are from this work, the ThU results are taken from ref. 24. For uranium in thorium it has been shown [25] that the  $T_c$  depression can be described well by a theory due to Kaiser [26] which predicts a decrease in  $T_c$  because of a diminishing strength of the attractive interaction. Subsequently it was borne out experimentally that for uranium in thorium this was largely due to an enhancement of the repulsive Coulomb interaction and that pair breaking due to



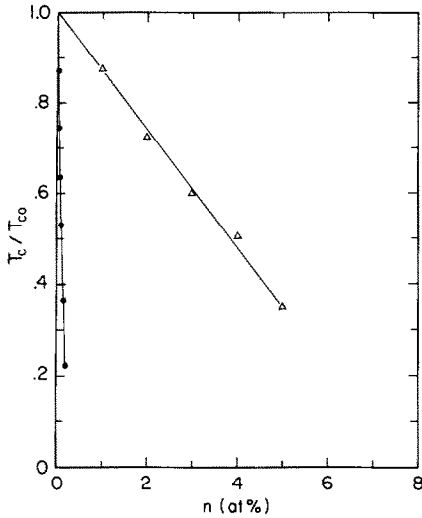


Fig. 7. Comparison of the depression of the superconducting transition temperature of ●,  $\text{Th}_{100-n}\text{U}_n$  and Δ,  $(\text{Th}_{1-n/100}\text{U}_{n/100})\text{Re}_2$  as a function of impurity concentration  $n$ .

possible magnetic interactions was negligible [24]. It is obvious from Fig. 7 that the  $T_c$  depression is very much weaker in our case and hence it can safely be concluded that no pair breaking due to local moments occurs in  $\text{Th}_{1-x}\text{U}_x\text{Re}_2$  for  $x < 0.05$ . Although  $\text{URe}_2$  has a strongly temperature-dependent magnetic susceptibility in its high temperature phase which has the same crystal structure as  $\text{ThRe}_2$ , uranium ions replacing thorium in  $\text{ThRe}_2$  do not seem to carry a well-defined moment at low temperatures.

All the experimental facts taken together confirm the above mentioned assumption that because of the short distance between the actinide sites in the crystal structure of  $\text{ThRe}_2$  and the high-temperature modification of  $\text{URe}_2$ , the 5f-electron states are itinerant in the latter. With decreasing temperature this narrow band of electron states becomes unstable with respect to a lattice distortion which subsequently results in the observed structural phase transition. This transition apparently induces changes in the topology of the electronic energy spectrum, removing parts with 5f symmetry from the Fermi energy. Finally we would like to mention that a previously reported [27] superconducting transition in  $\text{URe}_2$  could not be substantiated in subsequent experiments with additional specimens.

## References

- 1 H. R. Ott, H. Rudigier, Z. Fisk and J. L. Smith, *Phys. Rev. Lett.*, **50** (1983) 1595.
- 2 G. R. Stewart, Z. Fisk, J. O. Willis and J. L. Smith, *Phys. Rev. Lett.*, **52** (1984) 679.
- 3 H. R. Ott, H. Rudigier, T. M. Rice, K. Ueda, Z. Fisk and J. L. Smith, *Phys. Rev. Lett.*, **52** (1984) 1915.
- 4 D. J. Bishop, C. M. Varma, B. Batlogg, E. Bucher, Z. Fisk and J. L. Smith, *Phys. Rev. Lett.*, **53** (1984) 1009.

- 5 D. E. MacLaughlin, C. Tien, W. G. Clark, M. D. Lan, Z. Fisk, J. L. Smith and H. R. Ott, *Phys. Rev. Lett.*, *53* (1984) 1833.
- 6 H. R. Ott, H. Rudigier, Z. Fisk and J. L. Smith, *Phys. Rev. B*, *31* (1985) 1651.
- 7 H. R. Ott, H. Rudigier, P. Delsing and Z. Fisk, *Phys. Rev. Lett.*, *52* (1984) 1551.
- 8 Z. Fisk, G. R. Stewart, J. O. Willis, H. R. Ott and F. Hulliger, *Phys. Rev. B*, *30* (1984) 1249.
- 9 T. J. Heal and G. I. Williams, *Acta Crystallogr.*, *8* (1955) 494.
- 10 Q. Johnson, G. S. Smith and D. H. Wood, *Acta Crystallogr.*, *25* (1969) 464.
- 11 N. C. Bänziger and R. E. Rundle, *Acta Crystallogr.*, *2* (1949) 258.
- 12 F. A. Cafasso, H. M. Feder and D. M. Grün, *J. Chem. Phys.*, *38* (1963) 1256.
- 13 A. S. Wilson and R. E. Rundle, *Acta Crystallogr.*, *2* (1949) 126.  
C. W. Tucker, Jr., *Acta Crystallogr.*, *4* (1951) 425.  
W. T. Eeles and A. L. Sutton, *Acta Crystallogr.*, *16* (1963) 575.  
E. S. Fisher and H. J. McSkimin, *Phys. Rev.*, *124* (1961) 67.
- 14 B. A. Hatt, *Acta Crystallogr.*, *14* (1961) 119.
- 15 A. E. Dwight, *Trans. Am. Soc. Met.*, *53* (1961) 479.
- 16 M. B. Brodsky, R. J. Trainor, A. T. Aldred and D. H. Sowers, *J. Appl. Phys.*, *49* (1978) 1498.
- 17 K. H. J. Buschow and H. J. van Daal, in D. G. Graham and J. J. Rhyne (eds.), *Magnetism and Magnetic Materials-1971*, AIP, New York, 1972, p. 1465.
- 18 G. R. Stewart, *Rev. Mod. Phys.*, *56* (1984) 755.
- 19 A. L. Giorgi and E. G. Szklarz, *J. Less-Common Met.*, *22* (1970) 246.
- 20 C. A. Luengo, J. M. Cotignola, J. Sereni, A. R. Sweedler and M. B. Maple, in K. D. Timmerhaus, W. J. O'Sullivan and E. F. Hammel (eds.), *Proc. 13th Int. Conf. on Low Temp. Physics*, Plenum, New York, 1974, p. 585.
- 21 S. D. Bader, N. E. Phillips and E. S. Fisher, *Phys. Rev. B*, *12* (1975) 4929.
- 22 L. E. De Long, J. G. Huber, K. N. Yang and M. B. Maple, *Phys. Rev. Lett.*, *51* (1983) 312.
- 23 H. R. Ott, F. Hulliger, H. Rudigier and Z. Fisk, *Phys. Rev. B*, *31* (1985) 1329.
- 24 H. L. Watson, D. T. Peterson and D. K. Finnemore, *Phys. Rev. B*, *8* (1973) 3179.
- 25 M. B. Maple, *Magnetism*, *5* (1973) 289.
- 26 A. B. Kaiser, *J. Phys. C*, *3* (1970) 409.
- 27 H. R. Ott, F. Hulliger and Z. Fisk, *Bull. Am. Phys. Soc.*, *30* (1985) 408.