Title
Superconductivity in uranium compounds with Cu3Au structure.

Permalink
https://escholarship.org/uc/item/5w60r26r

Journal
Physical review. B, Condensed matter, 31(3)

ISSN
0163-1829

Authors
Ott, HR
Hulliger, F
Rudigier, H
et al.

Publication Date
1985-02-01

DOI
10.1103/physrevb.31.1329

Copyright Information

PHYSICAL REVIEW B VOLUME 31, NUMBER 3 1 FEBRUARY 1985

Superconductivity in uranium compounds with Cu_3Au structure

H. R. Ott, F. Hulliger, and H. Rudigier
Laboratorium für Festkörperphysik, Eidgenössische Technische Hochschule, Hönggerberg, 8093 Zürich, Switzerland

Z. Fisk
Los Alamos National Laboratory, Los Alamos, New Mexico 87545

(Received 5 September 1984)

Superconductivity has been observed in uranium compounds with partly disordered Cu_3Au-type crystal structure and interatomic U—U distances of more than 4 Å. Low-temperature specific-heat experiments reveal no anomalous enhancement of the electronic specific heat thus distinguishing the present materials from the unconventional superconductors UBe_{13} and UPt_3.

Until very recently, only a few uranium compounds were known to be superconducting at low temperatures, namely, U_6X compounds with X = Mn, Fe, Co, and Ni,[1,2] UCo,[1] and U_2PtC_2.[3] For elemental uranium, superconductivity is claimed for its γ (Ref. 3) and its α modification, but the latter under external pressure only.[4] In these materials superconductivity was ascribed to the formation of f-electron-derived energy bands due to direct $5f$-wave-function overlap between adjacent nearest-neighbor U atoms which are less than about 3.6 Å apart.[5]

Newer work on uranium intermetallics has shown that superconductivity is also possible when the U atoms are farther apart than 4 Å. So far, the most extreme example in this respect is UBe_{13},[6] where the nearest-neighbor U—U distance is 5.13 Å. In UPt_3 (Ref. 7) this distance is 4.13 Å, considerably larger than that found in the substances mentioned above. In these latter two cases, however, superconductivity develops out of a rather anomalous normal state and involves electrons with unusually heavy effective masses, giving rise to enormous electronic specific heats at low temperatures. For both UBe_{13} (Refs. 8 and 9) and UPt_3 (Ref. 9) it has been reasoned that superconductivity is not primarily due to conventional electron-phonon interaction, and therefore the superconducting state may be characterized by $l \neq 0$ paired electrons as opposed to the conventional $l=0$ BCS superconductors, where l is the electron-pair angular-momentum quantum number.

With these observations in mind, it seemed of interest to check whether the mentioned interatomic U—U distance is a crucial parameter in determining the low-temperature behavior of metallic uranium compounds and we also simply aimed at finding additional superconducting U compounds. In the course of this work we discovered superconductivity in U compounds crystallizing in the cubic Cu_3Au structure. Superconductivity was probed by measuring the magnetic susceptibility between 0.02 and 4 K, using a low-frequency ac mutual-inductance system with a primary-field amplitude of less than 0.1 Oe. For some of the compounds the magnetic susceptibility was also measured between 1.5 and 300 K, using a sample-moving magnetometer. In order to obtain values for the electronic specific-heat parameter γ, we also measured the temperature dependence of the specific heat between 1.5 and 12 K for two typical compounds. For further characterization we also measured the electrical resistivity ρ of three compounds between 1.5 and 300 K.

The samples were synthesized by arc melting under purified argon. The purity of the starting elements Al, Ga, Si, and Ge were 99.99% or better, that of Ru and Rh was 99.9% (Johnson-Matthey Co., London), and that of U was 99.7% with carbon as the main impurity. Of the materials studied (see Table I), UAl_2Si_2 and UAl_2Ge_2 had been reported by Zygmunt[10] to crystallize with primitive cubic cells and $a = 4.145(2)$ and 4.217(5) Å, respectively. From the experimental density we derive one formula unit per unit cell. This leads to $Pm\bar{3}m$ as the probable space group, i.e., a partly disordered perovskite or a Cu_3Au structure. The former structure, however, would require a much higher density. Thus we are left with the possibility of partially disordered Cu_3Au structures as met in $ThPd_4$ and UPd_4. In the case of UAl_2Si_2 the Guinier photographs indicated a slight variation of the lattice constant (see Table I). All UAl_2Si_2 powder patterns contained some foreign lines, though no lines from unreacted Si. The Guinier pattern of UAl_2Ge_2 revealed traces of free Ge in addition to the pure Cu_3Au-type phase. The same holds for the UGa_2Ge_2 sample which surprisingly had almost the same lattice constant as the corresponding Al compound.

Based on the lattice constants a_0 of the Cu_3Au end members UX_3(X = Al, Ga, Si, and Ge) and assuming the validity of Végard's rule, we would expect the observed lattice constants at the following compositions (with the $1a$ positions (0,0,0) fully occupied by U atoms only, and the X atoms statistically distributed on the $3c$ positions $(\frac{1}{2},\frac{1}{2},0;\frac{1}{2},0,\frac{1}{2};0,\frac{1}{2},\frac{1}{2})$: $UAl_{1.68}Si_{1.32}$ (4.145 Å), $UAl_{1.47}Si_{1.53}$ (4.163 Å), $UAl_{2.5}Ge_{0.5}$ (4.219 Å), and $UGa_{2.1}Ge_{0.9}$ (4.218 Å). In the case of the U-Al-Si compound one might accept this interpretation, but not for the U-Al-Ge and U-Ga-Ge phases. Since according to the x-ray photographs these latter phases only contained Ge as a second phase we measured their density δ with a pycnometer. For UAl_2Ge_2 we obtained $\delta = 7.73(6)$ g/cm^3. Assuming the sample to consist of a mixed

TABLE I. Relevant physical parameters of some U compounds with Cu_3Au-type crystal structure.

Substance	Sample No.	a_0 (Å)	T_c (K)	γ (mJ/mol K^2)	β (mJ/mol K^4)	Comments
UAl_2Si_2	91	4.145(5)	1.34 ±0.05	27.9	0.435	
	77	4.163(4)	not checked			
	99	4.176(6)	not checked			
UAl_2Ge_2		4.219(3)	1.60 ±0.10			
UGa_2Ge_2		4.218(3)	0.87 ±0.08			
URu_3		3.977(3)	0.145±0.005	12.4	0.413	partly disordered
URu_2Rh		3.977(4)	<20 mK			
USi_3		4.0348(8)	<20 mK			
UGa_3		4.256(3)	<20 mK			orders antiferromagnetically at 67 K

Cu_3Au-type phase and free germanium, $(U_xAl_{1-x})Al_{3x-1}Ge_{4-3x}+(5x-4)Ge$, the above experimental value for the density suggests a composition close to $(U_{0.82}Al_{0.18})Al_{1.46}Ge_{1.54}+0.1$ Ge. Unfortunately, the quality of the Guinier photograph was not sufficient to allow a clear choice based on the intensity of the diffraction lines. The pycnometric density for the U-Ga-Ge sample came out as 9.13(6) g/cm^3. For a Cu_3Au-type cell with one-quarter of the Au sites empty, $(U_{0.75}\square_{0.25})Ga_{1.5}Ge_{1.5}$, the calculated density would be $\delta=8.706$ g/cm^3, which is much too low, while for a perovskite-type distribution $UGa(Ge_2Ga)$ the calculated value $\delta=11.61$ g/cm^3 would be much too high. The observed density corresponds to a sample composition $(U_{0.87}Ga_{0.13})Ga_{1.6}Ge_{1.4}+(0.35)Ge$. However, we do not depend heavily on the correct composition of our Cu_3Au-type phases; this view is even more valid since we cannot completely exclude a small fractional occupation of the $1b$ position $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. Whatever the exact stoichiometry may be, the U—U distances are clearly greater than 4 Å which usually favors localized behavior of the uranium $5f$ electrons. Characterization of the binary Cu_3Au compounds was, of course, much less problematic than for the ternaries.

From measurements of the ac magnetic susceptibility, UAl_2Si_2, UAl_2Ge_2, UGa_2Ge_2, and URu_3 were found to be superconductors around and below 1 K. The experimental values for the superconducting transition temperature T_c are listed in Table I. We also investigated UGa_3, USi_3, and URu_2Rh which are, however, not superconducting above 0.02 K. The special case of UGa_3 will be further discussed below. The true composition of URu_2Rh may slightly deviate from the given stoichiometry (weight of the starting elements, 2.535 g; button after arc melting, 2.515 g; no chemical analysis). On the other hand, URu_2Rh may be a further example of an unexpected lattice-constant variation in a series of uranium alloys, certainly correlated with the electronic structure. It may also be noteworthy that URu_3 and URu_2Rh are both extremely hard, whereas the other compounds break rather easily.

In Fig. 1 we show the temperature dependence of the magnetic susceptibilities of URu_3 and UAl_2Si_2 between 4 and 280 K. Apart from these compounds which may be regarded as typical representatives of our binary and ternary Cu_3Au-type compounds, we also investigated and show the results of UGa_3 and USi_3. For all compounds we find an almost temperature-independent χ in this temperature range, indicating the absence of well-defined magnetic moments on the U ions in these materials, contrary to what one might expect from the lattice constant values. A somewhat unusual temperature dependence of χ for UGa_3, which has previously also been observed by Buschow and van Daal[11] with about 5% higher absolute values than ours, might suggest but certainly not indicate a magnetic phase transition below 100 K in this compound (see below). A comparison of the data in Ref. 11 with ours for USi_3 reveals that the former were probably obscured by impurities at lower temperatures since we do not observe the previously reported upturn below 150 K. The contribution of the free silicon in our sample can safely be neglected.[12]

If the temperature-independent χ's are interpreted as Pauli-type electronic magnetic susceptibilities, their values are rather large, however. It was therefore of interest to check whether the electronic specific heat might be equally enhanced at low temperatures, and we show the temperature dependence of the specific heats again of URu_3 and of UAl_2Si_2 between 1.5 and 12 K in Fig. 2. The c_p/T versus T^2 plot indicates that only at the lowest temperatures $c_p(T)$ may satisfactorily be represented by

$$c_p=\gamma T+\beta T^3\,, \tag{1}$$

where γ is the electronic specific-heat parameter and β

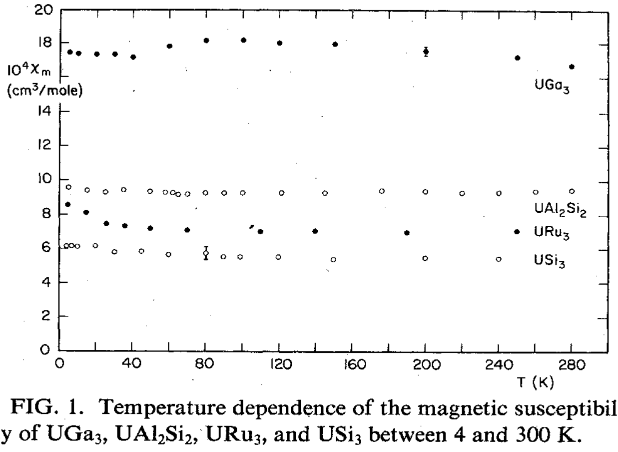

FIG. 1. Temperature dependence of the magnetic susceptibility of UGa_3, UAl_2Si_2, URu_3, and USi_3 between 4 and 300 K.

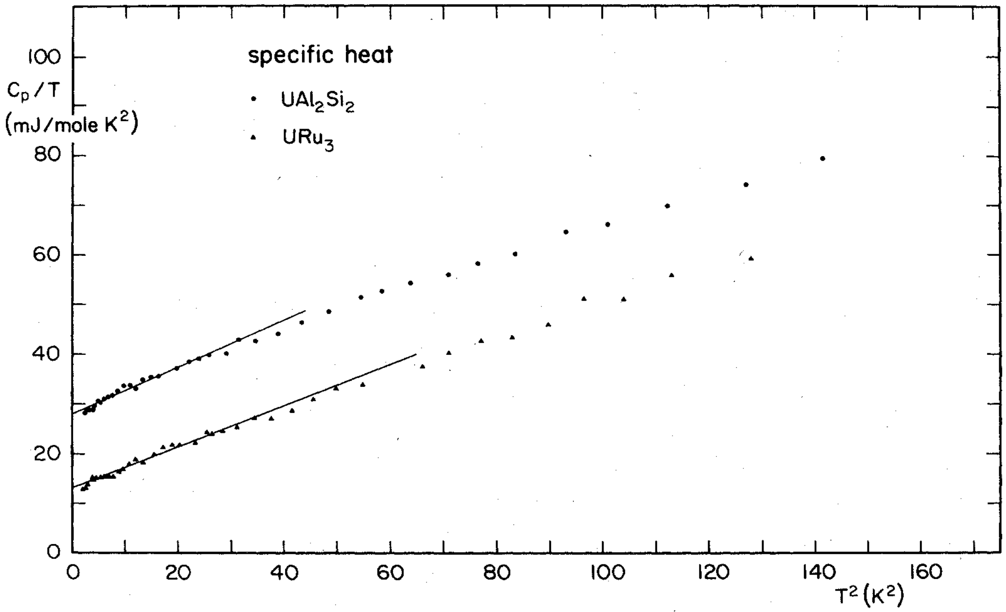

FIG. 2. Low-temperature specific heat of UAl_2Si_2 and URu_3 between 1.5 and 12 K.

determines the lowest-order contribution to the lattice. Obviously this T^3 term is almost identical for both compounds (see Table I). At higher temperatures we observe deviations from this simple behavior which are very similar to those recently reported for U_6Fe,[13] but have also been observed in Chevrel phases.[14] In Ref. 14 this temperature dependence of c_p/T was successfully reproduced with calculations, taking into account details of the electron-lattice interactions. We note that this temperature dependence of c_p is characteristically different from that reported earlier for binary U compounds with Cu_3Au structure.[15] The resulting γ values (see Table I) are obviously much smaller than what is obtained for UBe_{13} or UPt_3 (although in the latter case, the U—U distance is similar to our values), but of the same order of magnitude as those found in cubic NaCl-type U monopnictides and monochalcogenides[16] which also have similar nearest U—U distances but all order magnetically above 50 K. They are also comparable to the γ value of U_6Fe (Ref. 13) if that is renormalized to one U atom per mole. Finally it is quite interesting to note that the γ value for UAl_2Si_2 is half the sum of those of USi_3 (Ref. 17) and UAl_3 (Ref. 15).

A considerable difference is also observed in the general temperature dependence of the electrical resistivity between USi_3 and UAl_2Si_2. We show the results of our $\rho(T)$ measurements between 1.5 and 300 K for both these compounds in Figs. 3 and 4, respectively. As in ordinary metals, $\rho(T)$ of USi_3 decreases steadily on cooling and a residual resistivity ratio $\rho_{300}/\rho_{4.2}$ of about 100 is observed, much higher than what may be estimated from the data given in Ref. 11. Below 50 K, the observed temperature dependence of ρ is rather unusual, as may be seen from the expanded plot contained in Fig. 3. The data do not

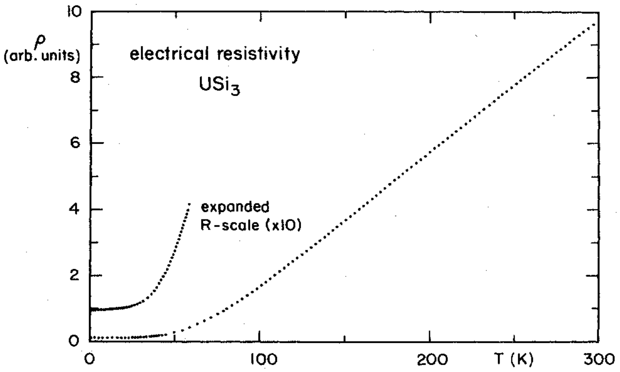

FIG. 3. Temperature dependence of the electrical resistivity of single-crystalline USi_3 between 1.6 and 300 K. ρ(300 K) is of the order of 20 $\mu\Omega$ cm.

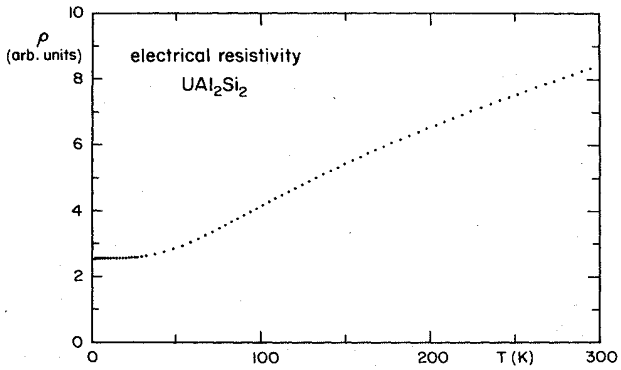

FIG. 4. Temperature dependence of the electrical resistivity of UAl_2Si_2 between 1.6 and 300 K.

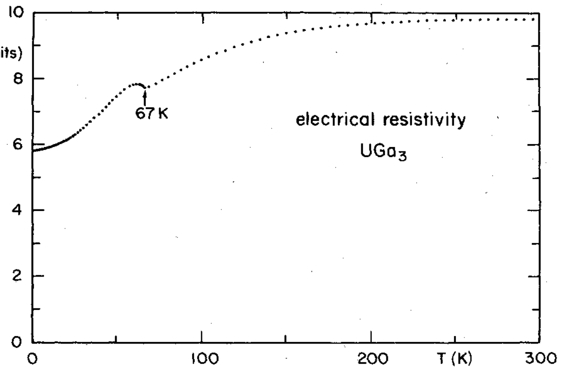

FIG. 5. Temperature dependence of the electrical resistivity of single-crystalline UGa_3 between 1.6 and 300 K.

yield a T^2 dependence of ρ in this temperature range as was reported in Ref. 11. These differences may be due to the fact that our sample was a flux-grown single crystal.

Turning to UAl_2Si_2, the absolute value of ρ is already higher at room temperature, as may be guessed from $\rho(T)$ of UAl_3.[11] As is expected for a disordered compound, ρ is not very much reduced upon cooling. In this case, the low-temperature resistivity follows a T^3 law rather than a T^2 law below 40 K, again characteristically different from the behavior of the binary compounds reported in Ref. 11.

Again in contrast to previously published data[11] is the T dependence we observe for ρ of UGa_3 below room temperature, measured on a single-crystal specimen. Starting from a room-temperature resistivity of the order of 100 $\mu\Omega$ cm, $\rho(T)$ decreases very slowly but with increasing positive $\partial\rho/\partial T$ upon cooling. At 67 K, ρ starts increasing again with decreasing temperature, passes through a maximum around 62 K, and finally reaches a still rather large residual resistivity at liquid-helium temperatures. The anomaly of the electrical resistivity below 67 K clearly indicates a phase transition which is, as established by neutron-diffraction experiments[18,19] of antiferromagnetic nature. The observation of this anomaly hence corroborates the claim of magnetic ordering in UGa_3 from previous neutron studies,[18,19] although the temperature dependence of χ is not indicative of that at all. Further studies with regard to details of the magnetically ordered state of UGa_3 might be very instructive.

In conclusion, we have found superconductivity in U compounds with Cu_3Au structure and nearest U—U distances of more than 4 Å. The normal-state properties resemble those of "enhanced" d transition metals, indicating that the f electrons in some way take part in the formation of itinerant electron states but do not show the anomalous behavior at low temperatures as, for example, in UBe_{13} and UPt_3. In this context it is interesting to note that the ratios of the experimental values of χ and γ are much larger for our superconducting substances than those found for UBe_{13} and UPt_3.

We find it remarkable that although the binary compounds UAl_3, USi_3, and UGe_3 are not superconducting, mixtures resulting in ternary compounds with disordered Cu_3Au structure are superconductors with critical temperatures close to or even above 1 K. Even more surprising is the fact that by starting from magnetically ordering UGa_3, a superconductor is obtained by replacing Ga with Ge, although, as mentioned above, the other binary end member is again not superconducting. Finally, our work implies that the atomic separation alone is not a reliable parameter for predicting the low-temperature behavior of U intermetallics.

Work performed in Switzerland was supported in part by the Schweizerische Nationalfonds zur Förderung der wissenschaftlichen Forschung. At Los Alamos work was done under the auspices of the U.S. Department of Energy. One of us (H.R.O.) would like to thank the Center of Materials Sciences at Los Alamos, where this work was completed, for financial support and his collaborators for their kind hospitality during the visit.

---

[1] B. S. Chandrasekhar and J. K. Hulm, J. Phys. Chem. Solids **7**, 259 (1958).
[2] H. H. Hill and B. T. Matthias, Phys. Rev. **168**, 464 (1968).
[3] B. T. Matthias, J. Phys. Colloq. C1-607 (1971).
[4] S. D. Bader, N. E. Phillips, and E. S. Fisher, Phys. Rev. B **12**, 4929 (1975).
[5] H. H. Hill, *Plutonium 1970 and Other Actinides,* edited by W. N. Miner (American Institute of Metallurgical Engineers, New York, 1970), p. 2.
[6] H. R. Ott, H. Rudigier, Z. Fisk, and J. L. Smith, Phys. Rev. Lett. **50**, 1595 (1983).
[7] G. R. Stewart, Z. Fisk, J. O. Willis, and J. L. Smith, Phys. Rev. Lett. **52**, 679 (1984).
[8] H. R. Ott, H. Rudigier, T. M. Rice, K. Ueda, Z. Fisk, and J. L. Smith, Phys. Rev. Lett. **52**, 1915 (1984).
[9] C. M. Varma, Bull. Am. Phys. Soc. **29**, 404 (1984); D. J. Bishop, C. M. Varma, B. Batlogg, E. Bucher, Z. Fisk, and J. L. Smith, Phys. Rev. Lett. **53**, 1009 (1984); D. E. MacLaughlin, C. Tien, W. G. Clark, K. Glover, M. D. Lan, Z. Fisk, J. L. Smith, and H. R. Ott, *ibid.* **53**, 1833 (1984).
[10] A. Zygmunt, in *Proceedings of the 2nd International Conference on Electrical Structure of Actinides Wroclaw, 1976,* edited by J. Mulak, W. Suski, and R. Trod (Polish Academy of Sciences, Wroclaw, 1976), p. 335.
[11] K. H. J. Buschow and H. J. van Daal, in *Magnetism and Magnetic Materials—1971 (Chicago),* proceedings of the 17th Annual Conference on Magnetism and Magnetic Materials, edited by D. C. Graham and J. J. Rhyne (AIP, New York, 1972), p. 1465.
[12] G. Busch and O. Vogt, Helv. Phys. Acta **33**, 889 (1960).
[13] L. E. DeLong, J. G. Huber, K. N. Yang, and M. B. Maple, Phys. Rev. Lett. **51**, 312 (1983).

[14] B. Lachal, A. Junod, and J. Müller, J. Low Temp. Phys. **55**, 195 (1984).

[15] M. H. van Maaren, H. J. van Daal, and K. H. J. Buschow, Solid State Commun. **14**, 145 (1979).

[16] H. Rudigier, H. R. Ott, and O. Vogt, *Proceedings of the International Conference on Rare Earth and Actinide Intermetallics, St. Pölten, 1984* [Physica B (to be published)].

[17] M. B. Brodsky, Rep. Prog. Phys. **41**, 1547 (1978).

[18] A.. Murasik, J. Leciejewicz, S. Ligenza, and A. Zygmunt, Phys. Status Solidi A **23**, K147 (1974).

[19] A. C. Lawson, A. Williams, J. L. Smith, P. A. Seeger, J. A. Goldstone, J. A. O'Rourke, and Z. Fisk (unpublished).