Magnetic and crystallographic structures in UTX intermetallic compounds

R.A. Robinson and A.C. Lawson
Los Alamos National Laboratory, Los Alamos, NM 87545 (USA)

V. Sechovsky and L. Havela
Charles University, Prague (Czech Republic)

Y. Kergadallan
Commission of the European Communities Joint Research Centre, Institute for Transuranium Elements, Karlsruhe (Germany)

H. Nakotte and F.R. de Boer
University of Amsterdam, Amsterdam (Netherlands)

Abstract

Uranium, together with other actinides and lanthanides, forms a large group of ternary intermetallic compounds of stoichiometry UTX (T≡transition metal, X≡p electron metal). These compounds are formed in several structure types and the occurrence and stability of particular structures with respect to the transition metal content suggests reasonable systematics. We have also investigated the magnetic structures of selected UTX compounds and it is revealing to relate the crystallographic and magnetic structures, because of the relationship between the magnetic symmetry and that of the U atom environment produced by the 5f–ligand hybridization, and the consequent anisotropic exchange. Those of ZrNiAl structure type are collinear, with moments along the hexagonal c axis. In the orthorhombic TiNiSi structure type, the moments are confined to the b–c plane (perpendicular to the uranium chains) and the structures are often incommensurate. In the hexagonal $CaIn_2$ (or GaGeLi) structure type, the magnetic structures form in an orthorhombic cell and, at least in the disordered centric group, again the moments lie perpendicular to the nearest-neighbour uranium spacing.

Uranium ternary compounds of composition UTX, where T is a transition metal element and X is a p electron metal, have been studied for some time [1, 2], with a view to understanding the role of 5f–d hybridization in the moment formation on the uranium site, and more specifically the magnetic anisotropy. A significant number of materials have now been studied (see Table 1) and some trends are beginning to emerge. Relatively little work has been done on the cubic UTX materials which form in the MgAgAs structure and in this article we concentrate on the more anisotropic hexagonal and orthorhombic structures. In the hexagonal ZrNiAl structure type (or its disordered analogue Fe_2P type), the nearest-neighbour U–U distance is in the hexagonal basal plane. In contrast, the other hexagonal system with GaGeLi structure type (or its disordered analogue $CaIn_2$ type) has the nearest-neighbour U–U distance along the c axis, that is, perpendicular to the hexagonal basal plane. Finally, the orthorhombic materials with TiNiSi structure type (or its disordered analogue $CeCu_2$ type) have nearest-neighbour distances

along the a axis. These nearest-neighbour distances are shown by the cigar-shaped links in Fig. 1 for each structure type. In all three cases, the nearest-neighbour distances are close to the Hill limit [3, 4] for uranium (3.5 Å), beyond which there will be negligible direct uranium–uranium overlap and where localized magnetic moments might be expected.

As an aside, we note that there is a sense in which the hexagonal basal plane of the ZrNiAl structure is related to the a–c plane of the TiNiSi structure. The former contains a network of triangles of U atoms, while the latter contains low amplitude zigzag chains of U atoms, as shown in Fig. 1. In Fig. 2, we show the more complicated PuRhAl structure [5], which is orthorhombic with the $Pd_{12}Mn_4Ge_8$ structure type [6]. The cell contains motifs from both the TiNiSi and ZrNiAl structures, and in some sense it is intermediate between the two. Kergadallan [5] has analysed this intermediate structure (which also occurs for PuIrAl) in terms of the variation of pairwise interatomic spacings for the PuTAl series (where T≡transition metal) and
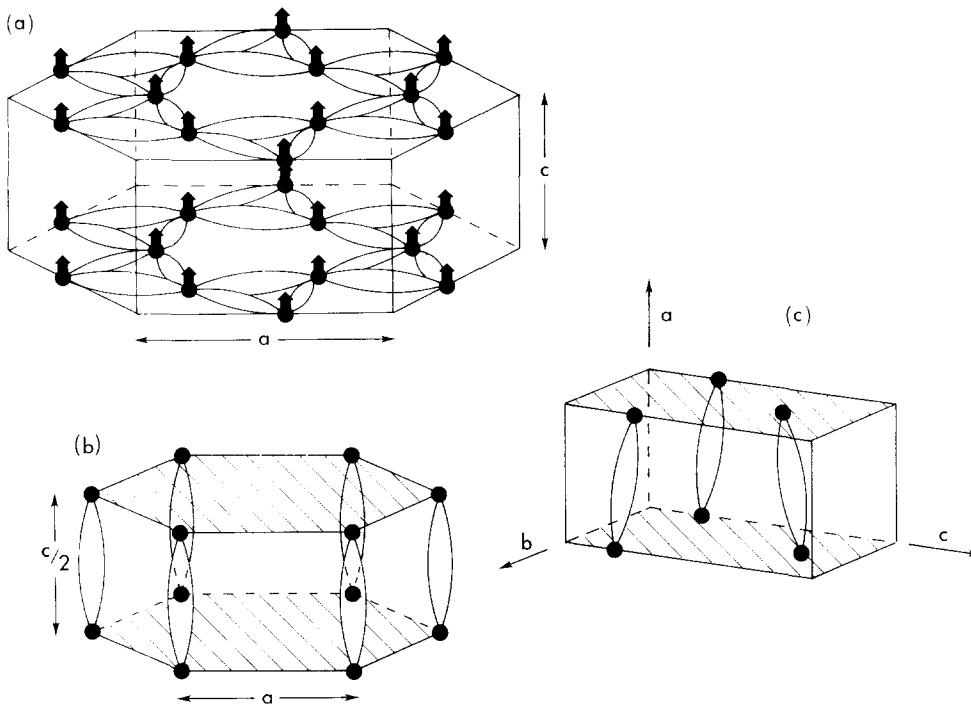
Fig. 1. Crystal structures of the three structure types described in the text: (a) ZrNiAl type (or Fe_2P if chemically disordered), (b) GaGeLi type (or $CaIn_2$ if chemically disordered) and (c) TiNiSi type (or $CeCu_2$ type if chemically disordered). In each case, for the sake of clarity, only the uranium atoms are shown. The "cigars" represent nearest-neighbour U–U distances, which are typically 3.6 Å. The arrows and shaded planes show the magnetic easy directions or planes, which are normally perpendicular to the nearest-neighbour vectors. In (b), only half (along the c axis) of the unit cell has been shown and similarly, in (c), only half (along the a axis) is shown.
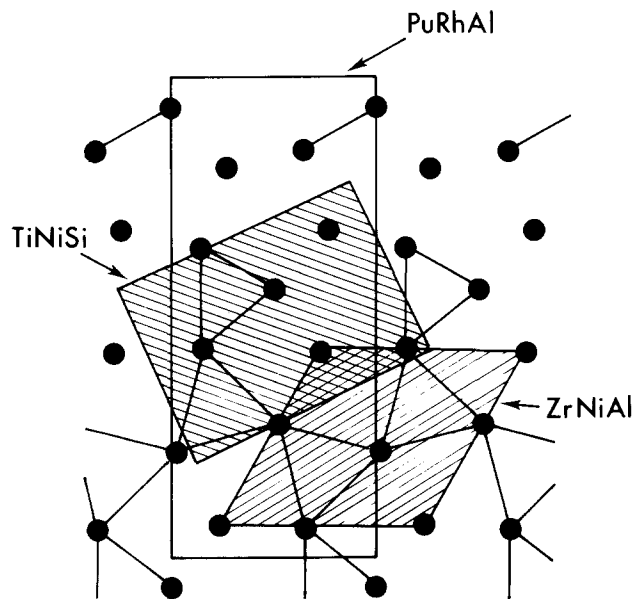

Fig. 2. Projection of the PuRhAl structure onto its $a–c$ plane, and the relation to the $a–c$ plane of the orthorhombic TiNiSi structure and the hexagonal basal plane of the ZrNiAl structure. The TiNiSi and ZrNiAl cells are shown by the shaded boxes, and in this case, all atoms in a given plane are shown. (After ref. 5.)

finds that this structure is stable for bond lengths intermediate between those of the ZrNiAl and TiNiSi structures.

In Table 1, we also compile the moment directions, as determined by neutron scattering or as inferred from magnetization data. In the case of the ZrNiAl type, the moments are typically along the c axis, that is perpendicular to the network of nearest-neighbour links. In addition, magnetization experiments on oriented and fixed powders show the c axis to be easy in all ZrNiAl-type compounds (except for a few compounds at the borderline of stability for the ZrNiAl structure) [22]. In the orthorhombic TiNiSi-type compounds, the moments typically lie in the $b–c$ plane, again perpendicular to the nearest-neighbour U–U links. Finally, a similar thing seems to be happening in the $CaIn_2$-type compound UAuSn: the moment lies in the hexagonal basal plane which is perpendicular to the nearest-neighbour U–U vector, which is along c [19]. In the other compound with this basic structure, UPdSn, the bulk susceptibility indicates that the c axis is the hard magnetic axis [23], which is consistent with the general trend in UTX compounds, but the detailed magnetic structure is more complicated, with both in-plane and out-of-plane components [18]. This case aside, the general trend is for the magnetic moments to lie in directions perpendicular

TABLE 1. UTX ternaries in which magnetic structures and/or anisotropy have been studied

Structure type	Compound	Comments	References
ZrNiAl, Fe$_2$P (hexagonal)	UCoAl	Orders if $B > 0.8$ T, c axis easy	7
	UNiAl	AF, C, μ along c	8
	UNiGa	AF, C, μ along c	9
	URhAl	F, μ along c	10
	URuAl	Does not order, c axis easy	11, 12
	UPdIn	Two magnetic phases, C, μ along c	11, 13
	UCoGa	Magnetic order (F or AF), c axis easy	14
TiNiSi, CeCu$_2$[a] (orthorhombic)	UNiGe	AF, C, μ in b-c plane	15, 16
	UPdGe	Two magnetic phases, μ in b-c plane	16
	UPtGe	AF, NC, IC, μ in b-c plane	16, 17
	UIrGe	AF?, no detectable moment	New results
GaGeLi, CaIn$_2$ (hexagonal)	UPdSn	AF, NC, no simple direction	18
	UAuSn	AF, C, μ in plane	19
MgAgAs (cubic)	UNiSn	AF, C, μ perpendicular to (100) ferromagnetic planes	20, 21

F, ferromagnet; AF, antiferromagnet; C, collinear; NC, non-collinear; IC, incommensurate.
[a]Note that the axis conventions are different in the TiNiSi (space group $Pnma$) and CeCu$_2$ (space group $Imma$) structures: the a and b axes are reversed. Throughout this article we use the TiNiSi ($Pnma$) notation.

to nearest-neighbour U–U vectors. This is also shown graphically in Fig. 1. In Fig. 1(a), the arrows signify the magnetic easy axis, while in Figs. 1(b) and 1(c) the shaded planes are magnetic easy planes. Note that, in all three figures, the magnetic easy planes or directions are perpendicular to the nearest-neighbour links.

This phenomenological observation might be rationalized using the arguments of Paixão et al. [10] developed for URhAl. In that case, these researchers have shown definitively that there is significant f–d hybridization in the hexagonal basal planes of the ZrNiAl structure, by observing induced magnetic moments on transition metal sites within the hexagonal plane containing uranium ions, but not on those out of this plane. In addition the magnetic moments point along the c axis. That is, the 5f–d hybridization is anisotropic with the strong component in the basal plane containing nearest-neighbour U–U directions, and the moments are perpendicular to that plane. Extending this idea to the other structures, one might argue that the TiNiSi structure compounds are strongly hybridized along the a axis, while CaIn$_2$-type materials such as UAuSn are strongly hybridized along the c axis.

Why then, might UPdSn deviate from this pattern? Our picture of the anisotropy in strongly hybridized UTX compounds is based on the anisotropic bonding of 5f electrons, and the exchange interaction within the hybridized planes or chains will be much stronger than that in perpendicular directions. However, in the case of UPdSn, there is good evidence from specific heat [23] and a form factor study [24] that UPdSn is quite localized in nature and that the f electrons are not strongly hybridized. So, in the case of UPdSn,

normal magnetic space group arguments, which allow a complicated canted structure with both in-plane and out-of-plane moment components, apply [18, 19].

On the contrary, UPtGe presents a case where such symmetry considerations do not seem to apply. The problem here is that UPtGe exhibits a complicated "cycloidal" magnetic structure in which the moments are confined to the b-c plane and rotate as one progresses along the b axis [16, 17]. This is perfectly consistent with our phenomenological description. However, the magnetic order parameter appears to be characteristic of a second-order transition [17] and magnetic symmetry arguments indicate that the order parameter should be one dimensional in this case [25], i.e. a moment-density wave. It is not. It should be noted, however, that uranium atoms are close to lying on a simple hexagonal lattice: the orthorhombic b/c ratio is almost exactly what it would be if hexagonal and then the uranium atoms are displaced alternately along the orthorhombic c axis. Another way of stating this is to say that the structure is closely related to the hexagonal AlB$_2$ structure type (Fig. 3). If the hybridization effects are strong enough, perhaps the interactions between the uranium chains are effectively those between magnetic "rods" arranged in a hexagonal pattern. Then, while the crystal structure is actually orthorhombic, magnetically the system behaves as if it is hexagonal.

Another trend that seems to be common to UTX compounds is that nearest-neighbour uranium atoms are ferromagnetically coupled. That is, the hexagonal layers in the ZrNiAl structure are ferromagnetically coupled within the plane, the a axis chains in the TiNiSi
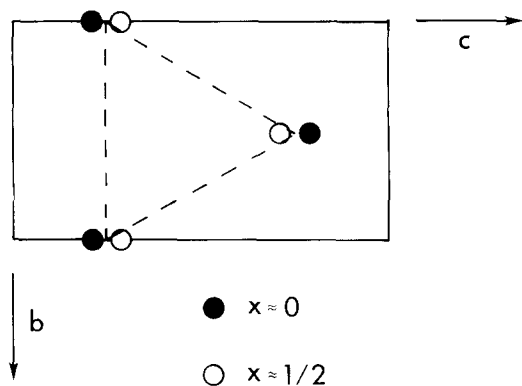
Fig. 3. Projection of the TiNiSi structure onto its b–c plane. For the sake of clarity, only the uranium atoms are shown. The dashed line represents distances between the uranium chains and they form an almost perfect equilateral triangle, by virtue of the fact that $c/b = 1.736$ (in the case of UPtGe [17]) $\approx \sqrt{3}$.

structure are ferromagnetically coupled within each chain and the c axis coupling in $CaIn_2$-type compounds is also ferromagnetic, except in the case of UPdSn. This is consistent with the theoretical ideas of Cooper et al. [26], who find that there is a tendency towards ferromagnetic interactions between nearest-neighbour Ce^{3+} ions in cerium intermetallic compounds. The heart of Cooper et al.'s theory is a hybridization-mediated two-ion interaction that leads to anisotropic exchange, and there is good reason to believe that the same ideas will apply to uranium compounds, even though they have more f electrons than Ce. Phenomenologically, much the same has been argued in the review by De Long et al. [27], who find that ferromagnetic structures are preferred for uranium intermetallic compounds with U–U spacings just beyond the Hill limit (3.5 Å $< d < 4.0$ Å). Both sets of researchers have concentrated mainly on cubic compounds where the anisotropy is less obvious than in the hexagonal and orthorhombic materials discussed here. Nevertheless, Cooper et al. [26] argue that, for cubic Ce compounds, planes of ferromagnetically coupled moments exist, with strong hybridization in the plane and the weak perpendicular hybridization, which leads to the moment being perpendicular to those ferromagnetic planes. This is, in fact, what occurs in the one cubic UTX compound which has been extensively studied, UNiSn [20, 21]. UNiSn orders in the type I f.c.c. antiferromagnetic structure, which has (100) ferromagnetic layers antiferromagnetically coupled to each other, and the moment is perpendicular to those ferromagnetic sheets. Not only is this consistent with Cooper's work on Ce compounds, but it is also consistent with the empirical trends we have identified in more anisotropic UTX compounds, in the sense that the moment is perpendicular to the ferromagnetically coupled planes, which are presumably strongly hybridized.

In summary, we have presented a phenomenology of trends in UTX ternary compounds. There seems to be fairly strong hybridization along the nearest-neighbour U–U directions, with ferromagnetic coupling in the same directions. The ordered magnetic moments are then almost universally aligned perpendicular to these directions. That is, there may be a systematic relationship between the hybridization anisotropy and the magnetic anisotropy, in which the unique axes are the same and the moments point along directions of relatively weak hybridization.

Acknowledgment

References

1 V. Sechovsky and L. Havela, in E.P. Wohlfarth and K.H.J. Buschow (eds.), Ferromagnetic Materials, Vol. 4, North-Holland, Amsterdam, 1988, Chap. 4.
2 V. Sechovsky and L. Havela, J. Magn. Magn. Mater., 104–107 (1992) 7.
3 H.H. Hill, in W.N. Miner (ed.), Proc. 4th Int. Conf. on Plutonium and Other Actinides, Santa Fe, NM, 1970, in Nucl. Metall., 17 (1970) 2.
4 K.G. Gurtovoi and R.Z. Levitin, Sov. Phys. Usp., 30 (1988) 827.
5 Y. Kergadallan, Ph.D. Thesis, Université de Paris XI, Orsay, 1993.
6 G. Venturini, B. Malaman, J. Steinmetz and B. Roques, Mater. Res. Bull., 16 (1981) 715.
7 M. Wulff, J.M. Fournier, A. Delapalme, B. Gillon, V. Sechovsky, L. Havela and A.V. Andreev, Physica B, 163 (1990) 331.
8 J.M. Fournier and P. Burlet, Proc. 21ème Journées des Actinides, Montechoro, 1991, p. 126.
9 H. Maletta, R.A. Robinson, A.C. Lawson, V. Sechovsky, L. Havela, L. Jirman, M. Divis, E. Brück, F.R. de Boer, A.V. Andreev, K.H.J. Buschow and P. Burlet, J. Magn. Magn. Mater., 104–107 (1992) 21.
10 J.A. Paixão, G.H. Lander, P.J. Brown, H. Nakotte, F.R. de Boer and E. Brück, J. Phys.: Condens. Matter, 4 (1992) 829.
11 V. Sechovsky, L. Havela, F.R. de Boer and E. Brück, J. Alloys Comp., 181 (1992) 179.
12 J.A. Paixão, G.H. Lander, A. Delapalme, H. Nakotte, F.R. de Boer and E. Brück, Europhys. Lett., 24 (1993) 607.
13 E. Sugiura, K. Sugiyama, H. Kawanaka, T. Takabatake, H. Fujii and M. Date, J. Magn. Magn. Mater., 90–91 (1990) 65.
14 H. Nakotte, F.R. de Boer, L. Havela, P. Svoboda, V. Sechovsky, Y. Kergadallan, J.C. Spirlet and J. Rebizant, J. Appl. Phys., 73 (1993) 6554.

15 A. Murasik, P. Fischer, R. Troć and V.H. Tran, J. Phys.: Condens. Matter, 3 (1991) 1841.

16 S. Kawamata, K. Ishimoto, Y. Yamaguchi and T. Komatsubara, J. Magn. Magn. Mater., 104–107 (1992) 51.

17 R.A. Robinson, A.C. Lawson, K.H.J. Buschow and J.W. Lynn, Phys. Rev. B, 47 (1993) 6138.

18 R.A. Robinson, A.C. Lawson, K.H.J. Buschow, F.R. de Boer, V. Sechovsky and R.B. Von Dreele, J. Magn. Magn. Mater., 98 (1991) 147.

19 R.A. Robinson, J.W. Lynn, V. Nunez, K.H.J. Buschow, H. Nakotte and A.C. Lawson, Phys. Rev. B, 47 (1993) 5090.

20 M. Yethiraj, R.A. Robinson, J.J. Rhyne, J.A. Gotaas and K.H.J. Buschow, J. Magn. Magn. Mater., 79 (1989) 355.

21 H. Kawanaka, H. Fujii, M. Nishi, T. Takabatake, K. Motoya, Y. Uwatoko and Y. Ito, J. Phys. Soc. Jpn., 58 (1989) 3481.

22 V. Sechovsky, L. Havela, H. Nakotte, F.R. de Boer and E. Brück, Rare Earth Research Conf., Monterey, CA, September 1993, submitted to J. Alloys Comp.

23 F.R. de Boer, E. Brück, H. Nakotte, A.V. Andreev, V. Sechovsky, L. Havela, P. Nozar, C.J.M. Denissen, K.H.J. Buschow, B. Vaziri, P. Meissner, H. Maletta and P. Rogl, Physica B, 176 (1992) 275.

24 S.W. Johnson, R.A. Robinson, H. Nakotte, E. Brück, F.R. de Boer and A.C. Larson, J. Appl. Phys., 73 (1993) 6072.

25 J. Rossat-Mignod, in K. Sköld and D.L. Price (eds.), Methods of Experimental Physics 23, Part C, Academic Press, Orlando, FL, 1987, p. 131.

26 B.R. Cooper, R. Siemann, D. Yang, P. Thayamballi and A. Banerjea, in A.J. Freeman and G.H. Lander (eds.), Handbook on the Physics and Chemistry of the Actinides, Vol. 2, North-Holland, Amsterdam, 1985, Chap. 6.

27 L.E. De Long, J.G. Huber and K.S. Bedell, J. Magn. Magn. Mater., 99 (1991) 171.