

MAGNETIC AND CRYSTALLOGRAPHIC STRUCTURES IN UTX INTERMETALLIC COMPOUNDS

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Abstract

Uranium, along 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 hybridisation, and the consequent anisotropic exchange. Those of ZrNiAl structure type are collinear, with moments along the hexagonal c-axis. In the orthorhombic NiSiTi 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 CaIn₂ (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 hybridisation on the moment formation on the uranium site, and more specifically the magnetic anisotropy. A significant number of materials have now been studied - see Table I - and some trends are beginning to emerge. In table I, we omit the cubic UTX materials which form in the MgAgAs structure and concentrate on the more anisotropic hexagonal and orthorhombic structures. In the hexagonal ZrNiAl structure type (or its disordered analogue Fe₂P 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 CaIn₂ 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 NiSiTi structure type (or its disordered analogue CeCu₂ type) has nearest neighbour distances along the a-axis. These nearest-neighbour distances are shown by the cigar-shaped links in Figure 1 for each structure type. In all three cases, the nearest neighbour distances are very close to the Hill limit[3,4] for uranium (3.5Å), beyond which there will be negligible direct uranium-uranium overlap and where localised magnetic moments might be expected.

In Table 1, we also compile the moment directions, as determined by neutron scattering or as inferred from susceptibility 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 the orthorhombic NiSiTi-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 CaIn₂-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[16]. In the other compound with this basic structure, UPdSn, the bulk susceptibility indicates that the c-axis is the hard magnetic axis[17], 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[15]. This case aside, the general trend is for the magnetic moments to lie in directions perpendicular to nearest-neighbour U-U vectors.

This phenomenological observation might be rationalised using the arguments of Paixao et al.[8] developed for URhAl. In that case, the authors have shown definitively that there is significant f-d hybridisation 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 out of plane. In addition the magnetic quantisation axis is along c. That is, there is strong

anisotropic hybridisation in the plane containing nearest neighbor 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 might be strongly hybridised along the a-axis, while CaIn₂-type materials like UAuSn should be strongly hybridised along the c-axis.

Why then, might UPdSn deviate from this pattern? The answer might lie in the fact that we have concentrated on the interactions between ions in the above treatment, but have neglected the sort of symmetry arguments that one might use in a Landau theory for localised moments. Such magnetic space-group arguments[15,16] have been shown to apply very well to UPdSn. There is also good evidence from specific heat [17] and a form-factor study[18] that UPdSn is quite localised in nature and that the f-electrons are not strongly hybridised. 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.

UPdSn presents a case where magnetic symmetry predominates over interactions. On the other hand, UPtGe is a case where the phenomenological description in terms of nearest-neighbour geometry and the consequent hybridisation seems to dominate over magnetic symmetry considerations. 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[13,14]. This is perfectly consistent with our phenomenological description. But the magnetic order parameter appears to be characteristic of a second-order transition[14] and magnetic symmetry arguments indicate that the order parameter should be one-dimensional in this case[19], i.e. a moment-density wave. It is not. Note 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 AlB₂ structure type - see Figure 2. If the hybridisation 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 would be 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 NiSiTi structure are

ferromagnetically coupled within each chain and interplanar coupling in CaIn_2 -type compounds is also ferromagnetic, except in the case of UPdSn .

In summary, we have presented a phenomenology of trends in UTX ternary compounds. There seems to be fairly strong hybridisation parallel to 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 hybridisation anisotropy and the magnetic anisotropy, in which the quantisation axes are the same and the moments point along directions of relatively weak hybridisation.

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Table I

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

Structure type	Compound	Comments	Reference
ZrNiAl / Fe ₂ P (hexagonal)	UCoAl	orders if B > 0.8T, c-axis easy	[5]
	UNiAl	does not order in field	[6]
	UNiGa	AF, C, μ along c	[7]
	URhAl	F, μ along c	[8]
	URuAl	does not order, c-axis easy	[9]
	UPdIn	AF, C, IC, μ along c	[9,10]
	UCoGa	magnetic order (F or AF), c-axis easy	[11]
NiSiTi / CeCu ₂ * (orthorhombic)	UNiGe	AF, C, μ along c	[12,13]
	UPdGe	2 magnetic phases, μ in b-c plane	[13]
	UPtGe	AF, NC, IC, μ in b-c plane	[13,14]
	UIrGe	AF?, no detectable moment	new results
GaGeLi / CaIn ₂ (hexagonal)	UPdSn	AF, NC, no simple direction	[15]
	UAuSn	AF, C, μ in plane	[16]

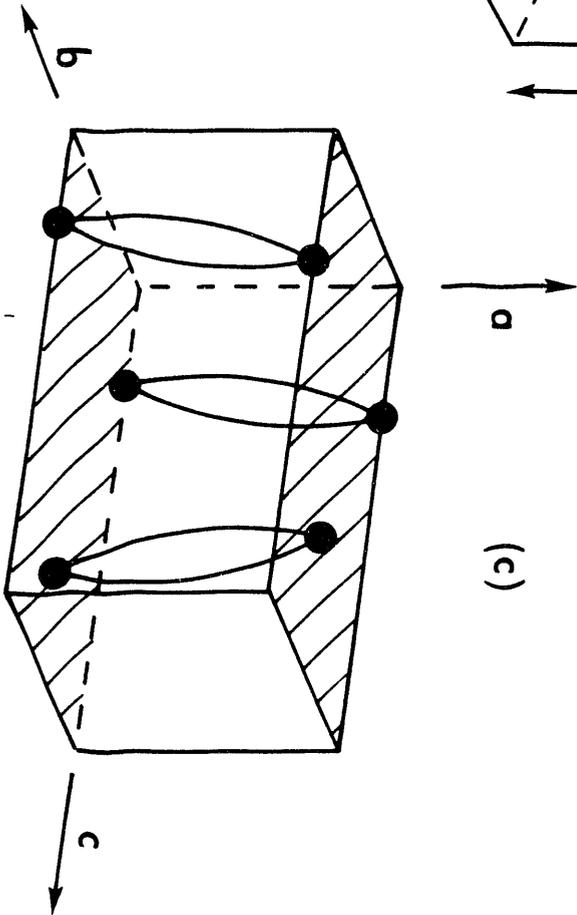
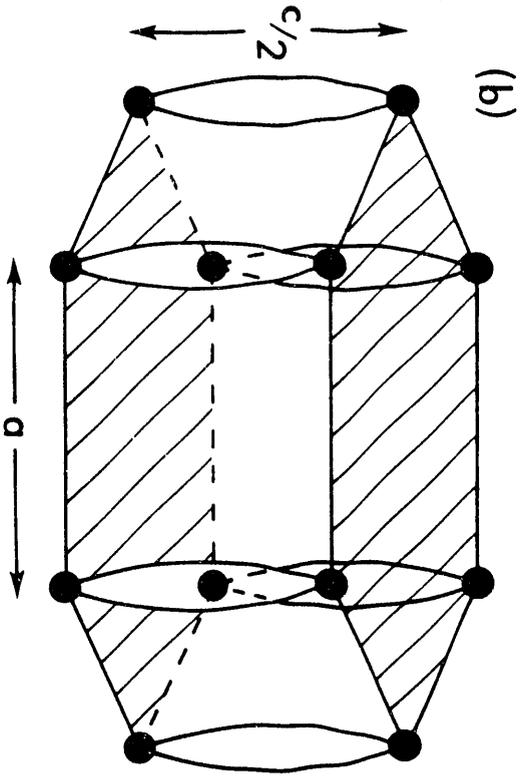
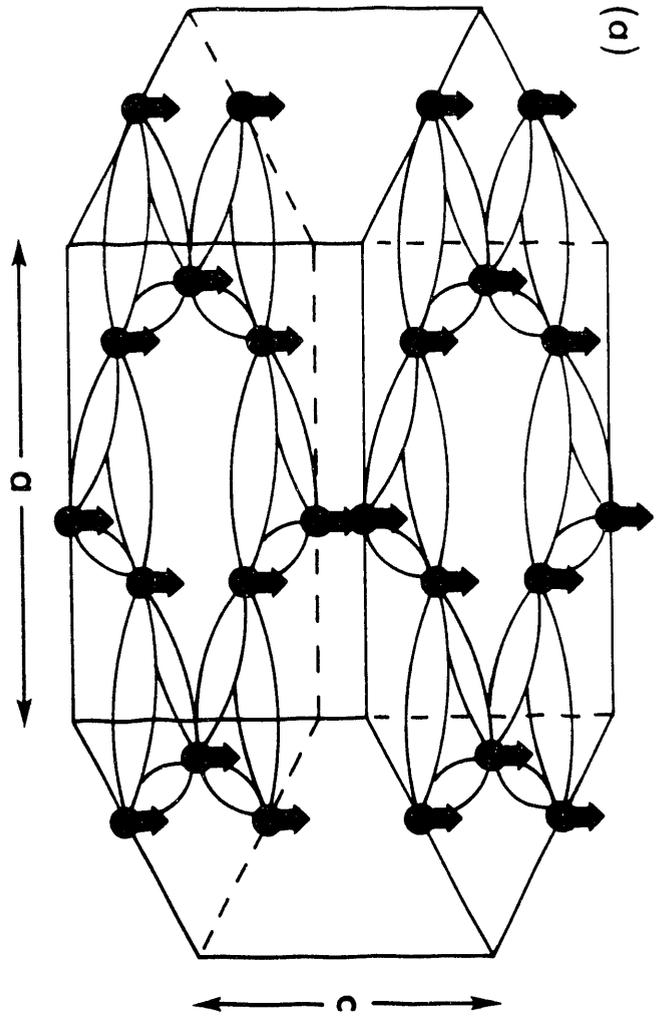
F = ferromagnet, AF = antiferromagnet, C = collinear, NC = noncollinear, IC = incommensurate

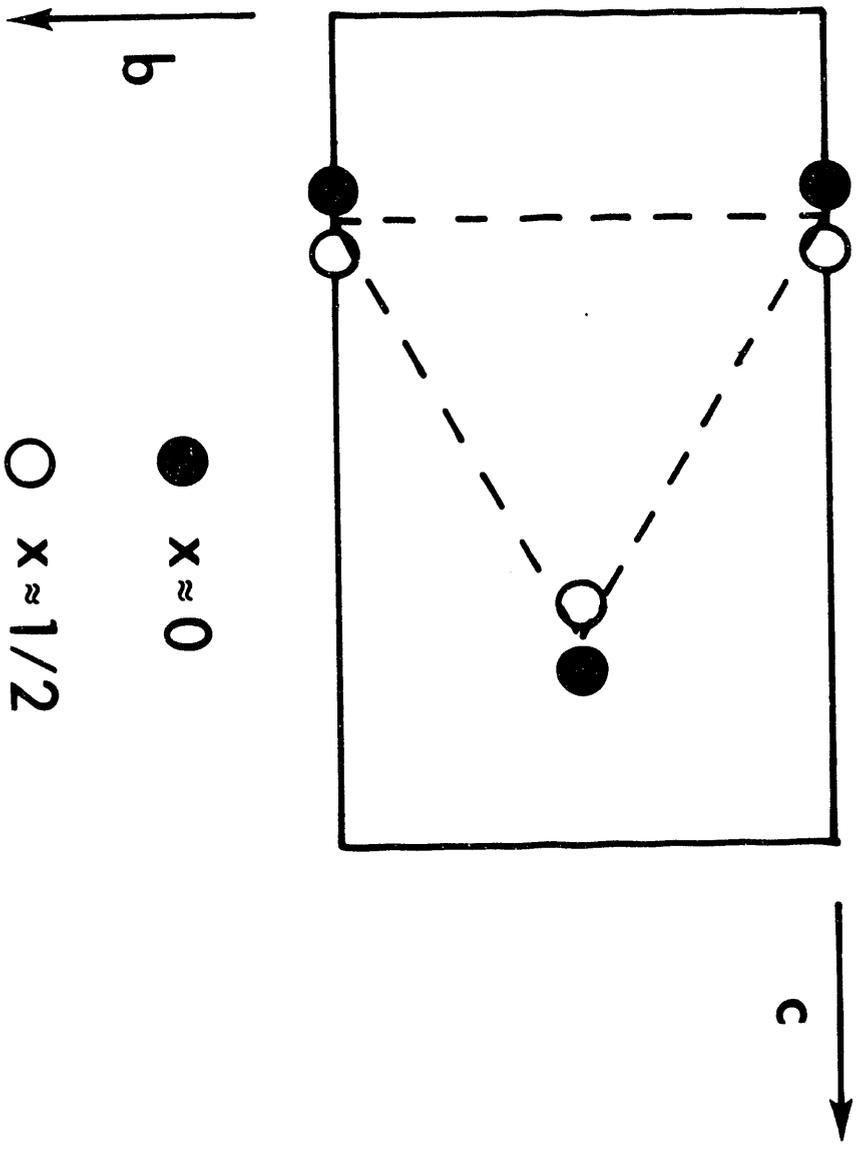
* Note that the axis conventions are different in the NiSiTi (space group Pnma) and CeCu₂ (space group Imma) structures: the a- and b-axes are reversed. Throughout this article we use the NiSiTi (Pnma) notation.

Figure Captions

Figure 1 Crystal structures of the three structure types described in the text: (a) ZrNiAl type (or Fe₂P if chemically disordered), (b) GaGeLi type (or CaIn₂ if chemically disordered) and (c) NiSiTi (or CeCu₂ 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 3.6Å. 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.

Figure 2. Projection of the NiSiTi structure onto its b-c plane. For the sake of clarity, only the uranium atoms are shown. The dashed lines represent 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 [14]) $\approx \sqrt{3}$.





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