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Similarities and Differences in the Physical Properties of Rare Earth and Uranium Intermetallic Compounds

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The compounds exhibiting the tetragonal $BaAl_4$ structure and its modifications represent one of the families of intermetallic systems that have turned out to be particularly numerous and interesting. Their general formula is RT_2X_2, where $R = f$ elements (4*f* or 5*f*), T = transition metals (3*d*, 4*d*, 5*d*), and X = silicon or germanium. All these compounds have metallic behavior, but different situations can occur according to the strength of the hybridization of the *f* states with the valence-band states: Pauli paramagnetism, mixed and intermediate valence states, spin fluctuations, Kondo state, heavy fermion state, and local moment magnetism. The general features of the rare earths and actinides are reviewed so as to illustrate these several physical properties, and a comparison between the rare earth and uranium systems is made.

Introduction

Since the 4*f* and 5*f* states play an important role in the physical properties of the rare earth- and actinide-based compounds, it is necessary for any discussion of their properties to recall the main atomic features of the elements. It is the degree of localization of the 4*f* and 5*f* states, reflected both in the spatial extension of the 4*f* and 5*f* orbitals and in the molar volume of the element, which mainly governs such physical properties as localized magnetism, Kondo-like, intermediate valence, and heavy fermion states, and also superconductivity.

General Features of Rare Earths and Actinides

The 4*f* electronic states are confined deeply in the core of the lanthanide ion and can be treated in most cases as localized. In contrast, for actinides and especially for uranium, the 5*f* electron wave functions are more extended than the 4*f* ones. It is also worth noting that the dependence of the molar volume on the atomic number *Z* of the light actinide series is similar to that found in the 3*d*, 4*d*, and 5*d* transition metal series for which the *d* states participate in the chemical bonding.

Indeed, a correct description of the electronic states of the light actinides is just between a localized and a band picture approach. The importance of the interatomic spacing with regard to the delocalization of 5*f* electronic states in U, Np, and Pu was raised by Hill (*1*). For interatomic spacings lower than a certain critical value (~3.5 Å for uranium) a nonmagnetic (and frequently superconducting) ground state is found as a consequence of a 5*f*–5*f* overlap and the resulting large delocalization of the 5*f* states. However, there are an increasing number

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of exceptions to Hill's rule. For example, although in the UX_3 compounds, where X = Si, Ge, Sn, and Pb, the U–U spacings are clearly higher than Hill's limit, nevertheless some of them exhibit a Pauli paramagnetism characteristic of a $5f$ delocalization. In this case a $5f$–ligand hybridization is a dominating mechanism controlling the delocalization and determining the $5f$ bandwidth.

The hybridization of the $4f$ or $5f$ levels with ligand orbitals determines the degree of delocalization of the f orbitals. This hybridization varies as the ratio of the electron transfer energy integral t and the excitation energy ΔE. A measure of the electron transfer energy integral is, qualitatively, the magnitude of the overlap integral for the cation and ligand orbitals. A simple analysis of the s, p, or d wave functions of the ligands shows, from a Taylor-series development, that only the cubic and higher order terms contribute to the overlap integral, that is to say (*2*)

$$\frac{1}{6}\sum_{xyz}\left(\frac{\partial^3\phi}{\partial r_x \partial r_y \partial r_z}\right)_{R_f} r_x r_y r_z,$$

where ϕ is the symmetrized s, p, or d wave function of the ligand and R_f the position of the actinide atom with respect to that of the ligand. Consequently, it is the spatial variation of the ligand orbitals rather than their extension that determines the magnitude of t and hence the strength of the f–ligand hybridization.

Furthermore, the matrix elements between an f orbital and a non-f ligand orbital from a neighboring site are generally small. The most pronounced effects are observed for actinides having a high coordination number in the crystal structure. Therefore the strength of the f–ligand hybridization will depend sensitively on the crystal structure of the compounds for a given ΔE.

It is not surprising if there is a great deal of parallelism between isostructural Ce and U compounds. These similarities result mainly from the following observations:

(i) In U-based compounds, a $5f$ level is generally close to or pinned at the Fermi energy.

(ii) in rare earth-based compounds, a $4f$ level is located close to the Fermi energy only for the anomalous lanthanides Ce, Sm, Eu, Tm, and Yb, which may have generally a valence different from three and varying as a function of both temperature and pressure; they differ clearly from the other rare earths, labeled "normal rare earths," for which the $4f$ levels are far from the Fermi energy (~5–10 eV).

(iii) the $4f$ orbital is more spatially extended for cerium than for the other rare earths.

The magnetic properties of Ce- and U-based compounds are typical of narrow-band metals, ranging from enhanced Pauli paramagnetism through spin fluctuations and Kondo-lattice behavior to itinerant magnetism.

From this discussion will be excluded compounds containing normal rare earths in which the magnetic $4f^n$ configurations are located far below the Fermi energy (~5–10 eV) and are magnetically coupled via a polarization of the conduction electrons (RKKY). In this indirect exchange mechanism the magnitude of the $4f$ moment remains preserved.

The magnetic behavior of Ce- and U-based compounds can be described simply by considering the exchange parameter J that characterizes the coupling between the spins of the conduction electrons (s) and the local magnetic moment (S),

$$J \propto \frac{|V_{d\text{-}f}|^2}{E_F - E_f},$$

where $V_{d\text{-}f}$ is a matrix element that admixes the conduction electron states and the localized f electron states. The energy difference in the denominator represents the energy necessary for promoting an electron from the *f* level to the Fermi energy.

According to the value of J, different physical situations can be encountered in concentrated magnetic systems.

For small J values, magnetic indirect exchange interactions of the Ruderman–Kittel–Kasuya–Yosida (RKKY) interactions (*3*), a magnetic ordering occurs, and the magnetic ordering temperature increases as J^2,

$$T_{\mathrm{RKKY}} \propto J^2/w,$$

where w is the width of the conduction band.

For higher J values, three behaviors can be encountered and distinguished by three parameters:

(i) The position of the f level (E_f) with respect to the Fermi level (E_F);

(ii) The Coulomb repulsion (U) between f electrons of opposite spin;

(iii) The width (2Δ) of the f level.

Magnetic properties of Some Intermetallic Compounds Containing Normal Rare Earths

In rare earth metallic compounds it is well known that a strong exchange indirect interaction exists between localized 4*f* via the conduction electrons. This interaction gives an oscillatory distribution of spin density in the region of the local moment. Very roughly, if a second atom bearing a local magnetic moment is situated at an arbitrary distance from the first, it interacts ferromagnetically or antiferromagnetically, depending on whether it is in a positive or a negative part of the polarization wave from the first atom. This interaction has a long range and oscillatory character and can show quite large variations of its strength and even reversal of its sign with small changes in the relationship between the interatomic distance and the periodicity of the spin density. Due to its nature, this interaction may give rise to very different magnetic structures: (i) simple collinear magnetic structures, (ii) non collinear magnetic structures with simple antiferromagnetic or ferromagnetic interactions in which a strong crystalline anisotropy superposed by the crystalline electric field plays an important role in stabilizing the direction of the moments via spin–orbit coupling, or (iii) magnetic structures that are incommensurate with the lattice due to competitive antiferromagnetic and ferromagnetic interactions arising from the oscillatory nature of the RKKY exchange: helimagnetic and modulated structures depending on the magnetic anisotropy (we do not discuss compounds with superexchange interactions).

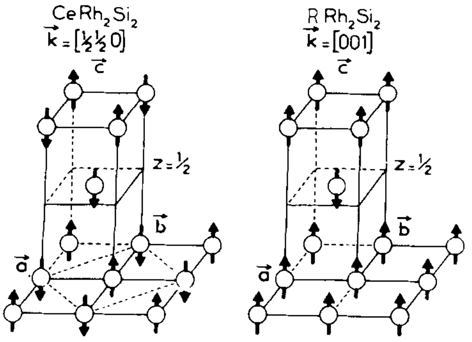

FIG. 1. Magnetic structures of RRh$_2$Si$_2$ (R = Nd, Tb; $\vec{k}$ = [001]) and CeRh$_2$Si$_2$ ($\vec{k}$ = [$\frac{1}{2}$ $\frac{1}{2}$ 0]).

The ternary silicides having the ThCr$_2$Si$_2$-type structure can illustrate nicely these different magnetic behaviors.

With normal rare earths (e.g., R = Nd, Gd, Tb, Dy, Ho, Er) RRh$_2$Si$_2$ and also RRu$_2$Si$_2$ with R = Nd and Tb exhibit a positive paramagnetic Weiss constant, indicating a predominance of the ferromagnetic interactions.

In the rhodium compounds, the magnetic moments have been found to be parallel to the *c* axis for Nd and Tb (Fig. 1) (*4*). From Dy to Er, the magnetic moments form an

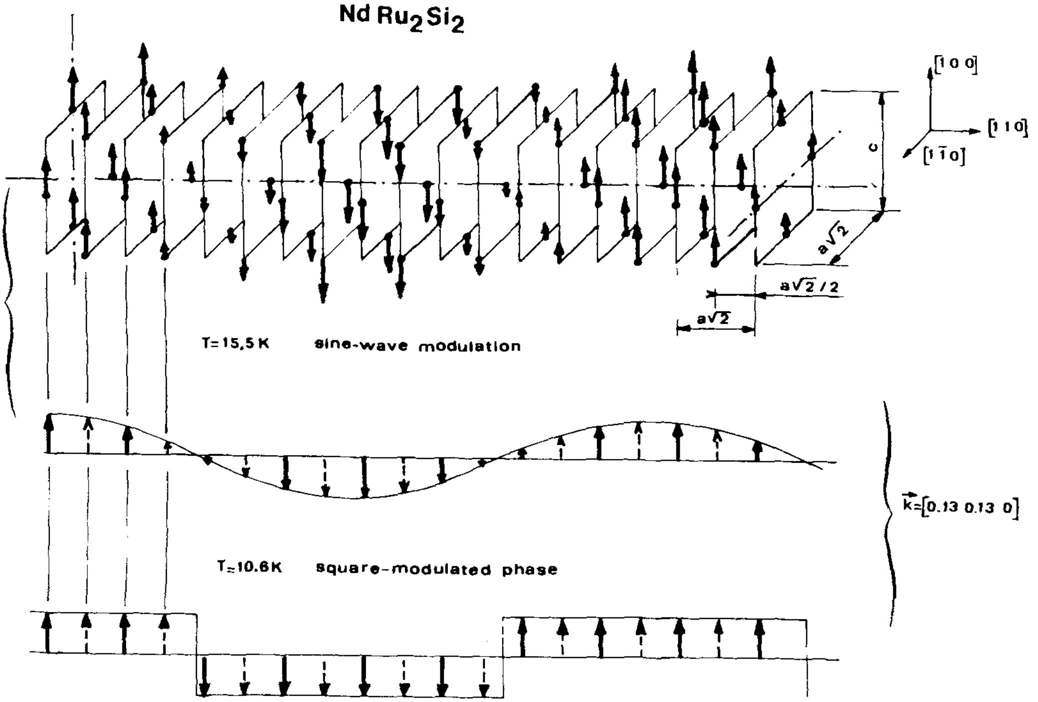

FIG. 2a. Schematic representation of the magnetic moments alignment of $NdRu_2Si_2$ for sine-wave and square-modulated phases.

angle with the c axis that increases on going down in the rare earth series, becoming perpendicular to the c axis with $ErRh_2Si_2$ (*5*, *6*). With Ru, which has one valence electron less than Rh, the magnetic behavior differs strongy from that observed with the rhodium compounds. For example, $NdRu_2Si_2$ shows a more complicated magnetic structure (Fig. 2a): below $T_N = 24$ K it develops a sine-wave modulation ($\vec{k}$ = [0.13 0.13 0]) of the magnetic moments always parallel to the c axis; a squaring of the magnetic structure occurs at about 15 K, and at $T < 10$ K a ferromagnetic order takes place with moments always along the c axis. $TbRu_2Si_2$ (Fig. 2b) also exhibits an incommensurate structure with $\vec{k}$ = [0.23 0 0]. Whereas just below $T_N = 55$ K the magnetic moments are modulated according to a sine wave, a squaring up of the modulation develops at lower temperature, giving rise to a square-wave modulation at $T = 3.1$ K (Fig. 2b) (*7*).

Kondo, Intermediate, and Mixed Valence States

Where the Coulomb repulsion *U and E_f are larger than the width of the f level* (2Δ), Kondo-type phenomena are found in systems with dilute concentrations of f-block atoms. Below a certain temperature T_K, called the Kondo temperature, the spins of the conduction electrons tend to compensate antiferromagnetically the spin of the f magnetic ions. This Kondo temperature varies exponentially with J according to the following expression:

$$T_K \propto \exp\left(-\frac{1}{N(E_F)J}\right).$$

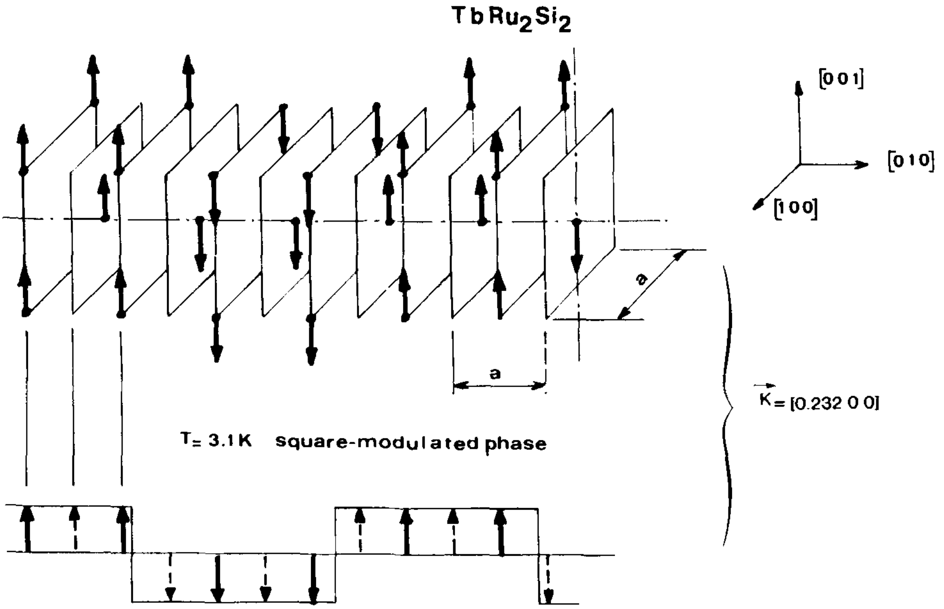

FIG. 2b. Schematic representation of the magnetic moments alignment of $TbRu_2Si_2$ for the square-modulated phase.

In concentrated magnetic systems the magnetic ions are not isolated as in diluted systems, and they can interact to give long range magnetic ordering. However, the RKKY magnetic interactions compete with the Kondo regime, and above a critical value of the exchange parameter J, the Kondo interactions begin to dominate and suppress the magnetic ordering, finally driving it to zero to put the system in a nonmagnetic ground state. The magnetic f ion always has integral valence.

As J increases, i.e., as the Kondo temperature increases, a nonintegral valence of the magnetic ion occurs. This situation, observed in some Ce-based compounds, is called an intermediate valence state. This valence fluctuation, which results from a quantum phenomenon, is characterized by a spin fluctuation temperature that, from the Heisenberg uncertainty principle, has the definition $T_{sf} \equiv h/k_B\tau_{sf}$. At temperatures much higher than T_{sf}, the temporal fluctuations of the magnetic moment are slow compared to the thermal fluctuations and the susceptibility becomes strongly temperature dependent, behaving like a Curie–Weiss law with Weiss constant of the order of T_{sf}.

The intermediate valence state does not involve a pinning of the f states at the Fermi level. From spectroscopic data it has been shown that the $4f$ level lies 1–2 eV below E_F and has a width $\Delta 4f \sim 0.1$–1 eV (e.g., $CePd_3$, $CeNi_2$). This intermediate valence state must be distinguished from the mixed valence state for which the f level is pinned at the Fermi level to give rise to nearly degenerate states like $4f^n(5d\text{–}6s)^m$ and $4f^{n-1}(5d\text{–}6s)^{m+1}$.

In this latter case, a nonintegral valence of the magnetic ion occurs depending on the temperature. This situation is accountered in anomalous rare earth compounds containing Sm, Eu, TM, or Yb. Contrary to the intermediate valence systems, the excitation energy is less than the width of the *f* level in a mixed valence system.

A careful examination of the values of the uranium effective moments in intermetallic compounds ranges generally from 2.54 to 3.58 μ_B/U, values expected for the $5f^1$ and $5f^2$ states, respectively. This observation does not require valence fluctuation behavior but is rather a result either of the inadequacy of the Russell–Saunders coupling or of 5*f*-band effects. In other words actinides are generally expected to fall into a coupling regime intermediate between *L–S* and *j–j* coupling.

The fact that U-based compounds having a strong 5*f*–ligand hybridization do not exhibit either an intermediate valence or a mixed valence state is likely due to a Coulomb energy repulsion $U = E_{5f}^{n+1} - E_{5f}^{n}$ which is relatively small and of the same order of magnitude as the width of the 5*f* level (2Δ).

Physical Behavior of Some Rare Earth Intermetallic Ternary Silicides

In order to illustrate these different physical behaviors, several systems have been chosen.

Let us examine the case of $CeIr_2Si_2$ which shows two crystal forms: $ThCr_2Si_2$-type at low temperature (I tetragonal) and $CaBe_2Ge_2$-type at high temperature (*P* tetragonal). The main goal of this study is to show the influence of the allotropic form on the cerium intermediate valence state (*8*).

The intermediate valence state of cerium is characterized by a double-peaked structure in the L_{III} X-ray absorption spectra (Fig. 3). From the intensities of X-ray absorption lines we can say that the intermediate valence state of cerium is more pronounced in the high temperature form than in the low one. This behavior is consistent with the Ce–(Si, Ir) distances, which are shorter in the high temperature form; shorter bond lengths give rise to a stronger 4*f* delocalization and therefore a more metallic behavior, as shown by the thermal variation of the resistivity.

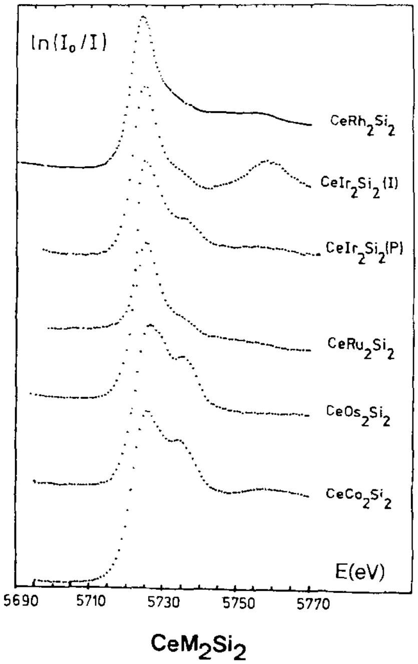

FIG. 3. Cerium L_{III} absorption edges at 300 K in CeT_2Si_2 silicides (*T* = Ru, Os, Co, Rh, Ir).

The L_{III} X-ray absorption spectrum of $CeIr_2Si_2$ is similar to that found for the intermediate valence compound $CeCo_2Si_2$ and differs from that observed for $CeRh_2Si_2$, which is characterized by a single absorption line corresponding to cerium in a pure trivalent state (*8*) (Fig. 3).

Contrary to metallic Ce-based systems, europium is in a mixed valence state in metallic Eu-based compounds like $EuIr_2Si_2$; the europium valence changes from 2.2 up to 2.8 as the temperature decreases from 300 K down to 4.2 K. The europium valence has been deduced from Mössbauer spectroscopy and magnetic measurements. Such a behavior has also been observed for the $EuCu_2Si_2$ and $EuPd_2Si_2$ compounds (*9*).

Valence instabilities occur in cerium-based compounds where the coupling constant J increases due to a decrease of the excitation energy or to an increase of the $V_{d\text{-}f}$ matrix element, which admixes the $4f$ and the conduction states. This increase in J can be achieved by playing either with applied external pressure or with chemical alloying.

$CeRh_2Si_2$ with the $ThCr_2Si_2$-type structure is a suitable starting material for illustrating the occurrence of valence instabilities by replacing Rh by Co or Rh by Ru.

By chemical alloying between $CeRh_2Si_2$ which orders antiferromagnetically (Fig. 1) and $CeCo_2Si_2$ which exhibits an intermediate valence state, we deal with the chemical pressure effect without changing the electron concentration. An increase of the f–d hybridization is reflected by the variation of the lattice parameters which deviate strongly from Vegard's law (*10*). Furthermore, similar to $CeRh_2Si_2$ studied under pressure, a depression of the Néel temperature of the solid solution $Ce(Rh_{1-x}Co_x)_2Si_2$ is observed due to an increase of the spin compensation as the molar volume decreases with increasing Co content for $x < 0.125$ (Fig. 4a). An intermediate valence state occurs for $x > 0.125$. It is characterized by a broad maximum in the magnetic susceptibility curves. Such an intermediate valence state has also been demonstrated by X-ray absorption measurements at the L_{III}–Ce absorption edges.

The antiferromagnetic to intermediate valence transition has been followed by specific heat measurements at very low temperatures. A clear enhancement of the electronic specific heat term γ occurs for $x = 0.125$–0.150, i.e., at the antiferromagnetic to intermediate valence transition (Fig. 4a). A question is if this transition occurs through a heavy fermion state although the highest γ value is not very large ($\gamma \sim 90$ mJ/mol. K^2 for $0.125 \leq x \leq 0.15$) (*10*).

On the other hand, chemical alloying between $CeRh_2Si_2$ and the heavy fermion compound $CeRu_2Si_2$ gives an antiferromagnetic to heavy fermion transition. In this case, an increase of Ru content in the solid solutions $Ce(Rh_{1-x}Ru_x)_2Si_2$ decreases the conduction electron concentration and consequently the Fermi energy level moves down. The outstanding feature of this system is a large increase of the γ electronic specific heat terms as the Ru content increases within the compositional range of the magnetic ordering state, i.e. for $0 \leq x \leq 0.40$. Such behavior is rather unusual, since high γ values are generally observed in heavy fermion systems that do not exhibit magnetic ordering (Fig. 4b) (*11*).

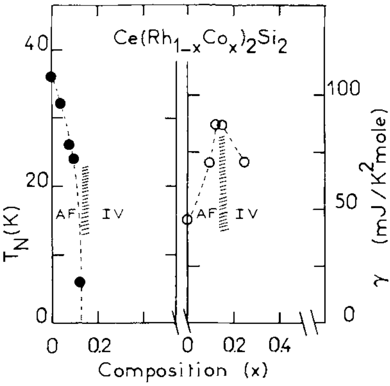

FIG. 4a. Néel temperature T_N and low temperature value of C/T ($= \gamma$) as a function of the Co content for $Ce(Rh_{1-x}Co_x)_2Si_2$ system.

CeT_2Si_2, UT_2Si_2 and UT_2Ge_2 Compounds

It is worth noting several similarities and differences in the magnetic behavior of isostructural CeT_2Si_2 and UT_2Si_2 compounds containing $3d$, $4d$, and $5d$ transition elements (*12–15*). For transition elements in the periodic table (T belonging to the columns VIII-A and I-B) the tendencies are the following as reported in Table I:

The f–d hybridization decreases from the left to the right as the number of valence electrons of the transition element increases. Thus, within a series, the systems

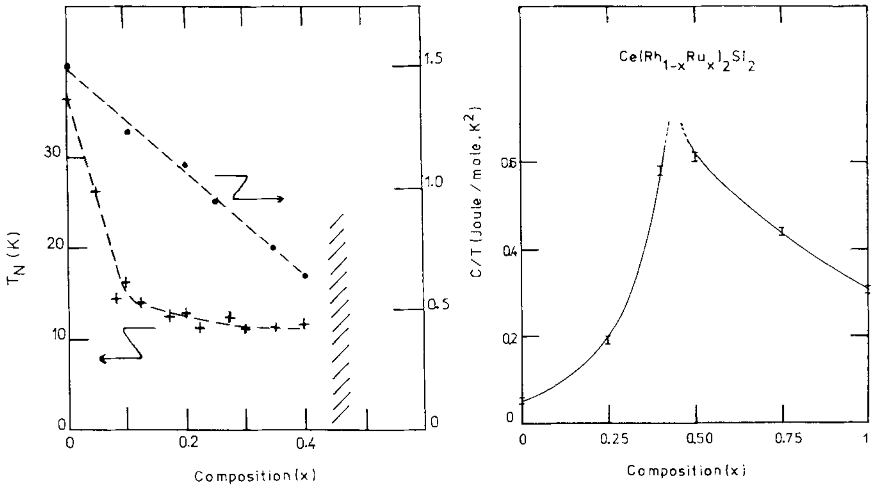

FIG. 4b. Néel temperature T_N and low temperature value of C/T ($=\gamma$) as a function of the Ru content for $Ce(Rh_{1-x}Ru_x)_2Si_2$ system.

with Ce move from an intermediate valence or heavy fermion state to magnetism and those with U move from Pauli paramagnetism via antiferromagnetism to canted antiferromagnetism. The negative and remarkably high values of the paramagnetic θp Weiss constant, which can be roughly associated with absolute values of the spin fluctuation temperatures, indicate an instability of the magnetic moments.

An intermediate valence state or Pauli paramagnetism is observed for compounds containing 3*d* and 5*d* elements, i.e., in systems for which the *f*–*d* hybridization is the strongest. These compounds exhibit the highest negative θp values. This behavior results from the shorter Ce– or U–ligand distances for the 3*d* elements and from the larger spatial extent of the 5*d* orbitals for the 5*d* elements.

In both Ce and U families, the Néel temperature with Rh is remarkably higher than those found in the other compounds.

Among the different compounds existing with both cerium and uranium, MT_2Si_2 families, five of them ($CeCu_2Si_2$, $CeRu_2Si_2$, $CePt_2Si_2$, URu_2Si_2, UIr_2Si_2) exhibit a heavy fermion behavior. The heavy fermion systems are mainly characterized by large values of the effective mass of the conduction electrons which is reflected in large values of both γ and χ.

Considering the evolution of the magnetic properties in a row of the periodic table, we can say that heavy fermion compounds lie at the borderline between antiferromagnetism and Pauli paramagnetism. However, there is an exception with URu_2Si_2, which exhibits, in addition to a heavy fermion state, both antiferromagnetic ordering and superconductivity (*16*).

It was interesting to show the influence of the nontransition element Si or Ge on the physical properties of the compounds within an isostructural UT_2X_2 family. With the replacement of Si by an element of larger size such as Ge, a weaker *f*–*d* hybridization could be expected due to an increase of the U–ligand distances. However, comparisons between the germanides and silicides are not yet possible, since the germanides are less well studied than silicides and are the sub-

TABLE I

Physical Behavior of CeT_2Si$_2$ of UT_2Si$_2$ Compounds

	$d_{(\overline{\mathrm{Ce}-T,\mathrm{Si}})}$(Å) Ce$T_2Si_2$				UT_2Si$_2$ (3.90 Å < $d_{\mathrm{u-u}}$ < 4.30 Å)			
3*d*	Fe	Co	Ni	Cu	Fe	Co^{AF}	Ni^{AF}	Cu^{F}
	IV	IV	IV	HF + SC	W.P.	T_N = 85 K	T_N = 103 K	T_C = 107 K
						θ_P = −285 K	θ_P = −56 K	θ_P = −11K
	3.127(I)	3.103(I)	3.106(I)	3.189(I)				
4*d*	Ru	Rh^{AF}	Pd^{AF}	Ag^{AF}	Ru^{AF}	Rh^{AF}	Pd^{AF}	
	HF	T_N = 37 K	T_N = 10.5 K	T_N = 9.5 K	HF + SC			
		θ_P = −61 K	θ_P = −57 K	θ_P = −36K	T_N = 17.5 K	T_N = 130 K	T_N = 97 K	
	3.218(I)	3.209(I)	3.248(I)	3.340(I)	θ_P = −160 K	θ_P = −40 K	θ_P = −10 K	
5*d*	Os	Ir	Pt	Au^{AF}	Os	Ir^{AF}	Pt^{AF}	Au$^{F/AF}$
	IV	IV	HF	T_N = 10 K		HF		
		3.208(I)	θ_P = −85 K	θ_P = −18 K	W.P.	T_N = 5.5 K	T_N = 36 K	T_N = 78 K
	3.207(I)	3.195(P)	3.235(P)	3.33(I)		θ_P = −156 K	θ_P = −57 K	θ_P = −36 K

Note. IV = intermediate valence state, HF = heavy fermion state, AF = antiferromagnetic, F = ferromagnetic, W.P. = weak paramagnetism; (I): $ThCr_2Si_2$-type structure, (P): $CaBe_2Ge_2$-type structure, SC: superconducting state.

ject of many discrepancies, the origin of which can be either in the existence of a nonstoichiometry or in the occurrence of a phase transformation.

For illustrating this point we have chosen the UT_2Ge$_2$ compounds with T = Co, Rh, and Ir.

According to different authors UCo_2Ge_2 of $ThCr_2Si_2$-type structure either orders antiferromagnetically at 170 K with a large negative θp value or does not exhibit magnetic ordering above 1.7 K (*17*).

$URh_{2-x}Ge_{2+x}$ displays a homogeneity range involving Rh and Ge sites. Magnetization and resistivity measurements characterize nondiluted Kondo behavior for $0.1 < x < +0.1$ with may be the occurrence of either a magnetic ordering or an onset of superconducting transition for $x = 0.1$ (*14, 15*).

Similar to URh_2Ge_2, UIr_2Ge_2 exhibits a small homogeneity range $UIr_{2-x}Ge_{2+x}$ with $-0.1 < x < -0.1$ and shows two allotropic forms both deriving from the $CaBe_2Ge_2$-type structure. The low temperature stoichiometric appears to order antiferromagnetically; the high temperature stoichiometric form exhibits a metamagnetic behavior (*14, 15*).

Conclusion

The results presented in this review of the RT_2X_2 compounds (R = rare earths or U, T = 3*d*, 4*d*, 5*d* elements) show that the occurrence of a particular magnetic structure may be explained by an interplay of exchange interactions described by the RKKY model and the anisotropy associated with the crystal electric field, which plays an important role mainly in the case of the light rare earth compounds. Cerium (4*f*) and uranium (5*f*) compounds show similarities and differences in their physical behavior depending on the position of the *f* level (E_f) with respect to the Fermi level (E_F), the Coulomb repulsion (U) between *f* electrons of opposite spins, and the width (2Δ) of the *f* level. The fact that U-based compounds do not exhibit a mixed valence state probably results from the very strong 5*f*–ligand hybridization. In this case, the Coulomb repulsion U is small and of the same order of magnitude as the width of the 5*f* level.

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