

Magnetic Properties of Uranium Compounds with Elements of the VA and VIA Groups. I. Compounds of UX Type*

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The magnetic properties of NaCl-type uranium compounds with group VA and group VIA elements are discussed. The assumption that J is a good quantum number is shown to be a good approximation for the ground multiplet of the uranium ion. The uranium ions are dealt with by the usual methods of crystal-field theory. They are assumed to be in the electrostatic field of their neighboring cations and conduction electrons and also to experience the exchange field of neighboring uranium ions. This model enables us to calculate the magnetic saturation moment in the ordered state and the susceptibility in the paramagnetic state. The results agree with experiment, except that the calculated (paramagnetic) magneton numbers of the Uvi compounds are higher than those measured. The computed (total) splittings of the ground state in those compounds are between 500 and 1200 cm^{-1} . The exchange interaction is derived from the Ruderman-Kittel-Kasuya-Yosida type of interaction and is used to explain the occurrence of the observed ferromagnetic and antiferromagnetic (type-I) ordering. The problems involved in such a model are discussed at length. A schematic band structure is proposed, the effective conduction electron mass being computed to be $3-9m$, while the s - f coupling constant is $12-22 \text{ eV } \text{\AA}^3$, appreciably larger than in lanthanide compounds.

I. INTRODUCTION

RECENT research in the field of magnetic properties of actinide compounds seems to justify an attempt to correlate and explain the interesting results obtained. The partially filled $5f$ shell in the actinides gives rise to the magnetic behavior of actinide alloys and compounds. To a certain extent there is an analogy with the lanthanides, but the $5f$ electrons are less concentrated around the nucleus than the $4f$ ones in the rare-earth atoms. As most of the actinides are radioactive and difficult to procure, the experimental work has concentrated mainly on uranium compounds and alloys.

Metallic uranium is paramagnetic and does not order magnetically at low temperature and even becomes superconductive below $T_c = 0.6^\circ\text{K}$. However, many of its compounds, especially those with elements of group VIA (S, Se, Te) and of group VA (N, P, As, Sb, Bi) show magnetic ordering. We shall denote by v an element of group VA, and by vi an element of group VIA. A large part of the data on these compounds is due to the pioneering work of the Polish group under Trzebiatowski. A consistent picture has now emerged, namely that Uvi and U_3v_4 compounds are ferromagnetic, while the Uv , Uv_2 , and UOvi are antiferromagnetic. We shall discuss here the comparatively simple case of the Uv and Uvi compounds, while the other compounds will be the subject of following papers.

All the Uv and Uvi compounds crystallize with the NaCl structure and some of their properties are tabulated in Table I. UO is apparently unstable.¹ The magnetic parameters of the compounds are comparatively independent of the nature of the anion present, thus confirming that the magnetic properties

are due mainly to the uranium ion. As the distance between the ions is large (between 3.5 and 4.4 $\text{\AA}$) it seems unlikely that direct interaction between the uranium ions is the cause of the magnetic ordering. It therefore appears probable that an indirect mechanism, like the Ruderman-Kittel-Kasuya-Yosida (RKKY) coupling, is operating. This conjecture is made more plausible by the relatively high electric conductivity of the compounds, which is only an order of magnitude lower than that of metallic uranium. It seems that the structure of the compounds can be described as consisting of uranium ions, probably in the U^{4+} state in all UX compounds, surrounded by anions and a cloud of conduction electrons. The model we propose is based on the following assumptions: (1) The magnetic moments observed are, primarily, due to the localized $5f$ electrons on the uranium ions; (2) the coupling mechanism between the magnetic dipoles takes place via the conduction electrons. Similar models have been proposed for lanthanide metals² and their compounds.³ We shall use our model to discuss the magnetic moments in the ordered and in the paramagnetic states, the type of order observed, and the electric properties of the compounds. It is to be expected that such a simplified model will only be a first approximation of the true state of affairs.

II. URANIUM ION

The model we use is a uranium ion surrounded by anions and conduction electrons. The site symmetry is octahedral and the behavior of such an ion can be analyzed by the well-known methods of crystal-field theory. The determination of the ionization state of the uranium ion in the UX compounds is a difficult task. Lanthanides appear mainly as trivalent, more rarely as divalent; but uranium can appear in several

* A concise report on this work was presented at the International Congress on Magnetism, Boston, 1967; J. Grunzweig and M. Kuznietz, *J. Appl. Phys.* **39**, 905 (1968).

¹ R. F. Stoops and J. V. Hamme, 65th Annual Meeting Am. Ceramic Soc., Pittsburgh, Pa., 1963, quoted by B. Cunningham, *Ann. Rev. Nucl. Sci.* **14**, 334 (1964) and by W. Price, *Can. Metal. Quart.* **3**, 183 (1964).

² R. J. Elliott, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1966), Vol. IIA.

³ S. Methfessel, *Z. Angew. Phys.* **18**, 414 (1965).

different valency states. Neither neutron diffraction work nor magnetic measurements have so far given a clear answer in the cases considered here. We shall, therefore, try to make a decision in the light of evidence available.

The radius of the 5f electronic shell, as derived from computed wave functions, is about 0.5 Å,⁴ while the available neutron diffraction data give about 0.45 Å.⁵ This should be compared with about 0.3 Å for the radius of the 4f electrons in gadolinium.

Compared with the rare-earth ions, the larger radius of the 5f shell in uranium might cause a partial overlap with the electron clouds of close neighbors and a mixing-in of their ligand wave functions into the 5f wave function, hence giving rise to bonding effects, covalency, and superexchange as they occur in the transition-metal ions. In our discussion of the uranium ion we shall draw on the recent review of the field by Wybourne.⁶ As a first approximation we assume pure Russell-Saunders (RS) coupling and a crystal-field interaction term which is much weaker than the spin-orbit coupling—that is, the usual assumptions employed in elementary discussions of rare-earth ions. However, the relative increase in strength of the spin-orbit coupling, compared with the electrostatic interaction terms within the ions, will cause a significant breakdown of the RS coupling rules; one then has to consider the presence of intermediate coupling.

This is shown in Table II, which also contains, for purposes of illustration, data on analog lanthanide ions. As far as our computations are concerned, the breakdown has a double effect: first, it changes (slightly) the energy separation of the lowest excited multiplet, which is of negligible consequence as far as the magnetic properties are concerned at the temperatures commonly employed. Second, because of the departure from the pure RS coupling rules, spin-orbit interaction mixes into the ground multiplet wave functions of higher states, mainly from states with the same J and with L and S differing by 0 or ± 1 . Because of mixing, the states lose their simple labeling scheme by the L , S , and J quantum numbers. However, in the case of uranium, the mixing of the ground state is comparatively small (especially when compared with heavier actinides), so that it is still justifiable to characterize it by the L , S , J numbers of its major component.

Apart from the considerations mentioned above, one must also take into account interaction terms, neglected so far, which arise between configurations. These terms

can appreciably affect the energy levels and wave functions if the configurations happen to be close together. Fairly extensive computations, mainly by Judd, Wybourne, and their collaborators, have established the structure of the ground state of some f^n ions. In Table III we show the results for different ionization stages of uranium and certain analogous ions.

Inspection of Table III shows that the admixture of states is never more than 10%. As far as the magnetic properties are concerned, we must also consider the change in the effective g of the ground level. This is tabulated in Table III. The changes in g are very small, less than 5%. The effects of configuration mixing are much stronger in the excited levels and also in transuranic elements, but the ground state of the uranium ions is not appreciably affected.

Of greater consequence is the fact that the crystal-field interaction terms in actinides are larger than those of the lanthanides, and hence not negligible in comparison with the spin-orbit ones.

This causes the breakdown of the crystal-field "rare-earth" approximation scheme, where strong spin-orbit splitting ($\sim 1000 \text{ cm}^{-1}$ in lanthanides) are assumed (which determine the structure and energy of the multiplets), and where the crystal field is only an additional small perturbation (less than 100 cm^{-1}). In the case of the actinides, the crystal-field terms are not negligible, and cause serious perturbations of the levels, so that the situation slightly resembles that found in transition-metal ions (though there the crystal-field terms are even more powerful, as compared with the spin-orbit terms). The usual treatment (by means of perturbation theory) breaks down and a rigorous diagonalization of a matrix, including all these terms simultaneously, should be attempted.

Such calculations have already been carried out in the case of some lanthanide and actinide ions, but they are only justified, for example, in cases of optical spectra, where a larger number of lines contains ample information. In such cases, the vast labor required enables one to optimize the many parameters which are not known theoretically, but computed to obtain a good fit for the experimental results. In our case, the paucity of data available hardly justifies such an approach at this stage. Furthermore, our interest is focused on the ground state, where the departures from the simple RS model are relatively small.

III. CRYSTAL-FIELD AND MAGNETIC COUPLING

The uranium ions are simultaneously exposed to the influence of the electrostatic field of adjoining anions and conduction electrons ("crystal field") and to the exchange-like magnetic interactions with neighboring cations. The nature of the magnetic coupling will be dealt with in a later section.

The magnetic data seem to fit best the case of U^{4+} , but we shall consider other possible ionization states. Uranium appears as U^{2+} (f^4 or $f^3 6d^1$), U^{3+} (f^3), U^{4+} (f^2),

⁴ F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Inc., Englewood Cliffs, N.J., 1963); J. T. Waber (private communication); C. J. Lenander, *Phys. Rev.* **130**, 1035 (1963).

⁵ UN: N. A. Curry, *Proc. Phys. Soc. (London)* **86**, 1193 (1965); UP: **89**, 427 (1966); S. Sidhu, W. Vogelsand, and K. D. Anderson, *J. Phys. Chem. Solids* **27**, 1197 (1966). UAs: R. Troć, A. Murasik, A. Zygmunt, and J. Leciejewicz, *Phys. Status Solidi* **23**, K123 (1967); UAs₂: A. Olès, *J. Phys. (Paris)* **26**, 561 (1965).

⁶ B. G. Wybourne, *Spectroscopic Properties of Rare Earths* (Interscience Publishers, Inc., New York, 1965).

TABLE I. Properties of UX compounds. a_0 is the lattice constant; U-U the spacing between adjoining uranium ions; Type refers to the type of antiferromagnetic order present at low temperature; T_c (or T_N) is the transition temperature; n_f (or n_a) is the observed magnetic moment in the ordered state (in Bohr magnetons), while n_p is that in the paramagnetic state; θ is the paramagnetic Curie temperature (Weiss's parameter); ρ is the electric resistivity and R_H the Hall-effect constant; γ is the linear term in the (low-temperature) specific heat (the "electronic-specific-heat" constant).

(a) Ferromagnetic compounds.													
Compound UX	a_0 (Å)	U-U (Å)	T_c (°K)	n_f (μ_B)	χ (300°K) (10^{-6} cgs emu) χ_g χ_M	n_p (μ_B)	θ (°K)	T (°K)	ρ ($\mu\Omega$ cm)	R_H (cm^3/C)	γ (10^{-4} cal/ mole deg ²)	References	
US	5.487	3.88	178±2	1.20	4180	2.22	+173	300	112-360	+0.0006	49	a-1	
	5.4885				4600				235; 286; 360	(0.45 h/U)			
	5.489		180±5	(1.60)	20.9	5667	2.25±0.05	+185	1300	328; 430		m, n, p	
USE	5.710	4.07	160.5	1.31	22.5	7133	2.51	+188	80	120	20.8	g, j, o-s,	
	5.7435		187±2					300	600; 244; 280	+0.008			
	5.750		210					1000	750				
UTe ^{aa}	6.151	4.35	103	1.10	14.3	5230	2.84	+104	80	1200	+0.2	g, r-u	
	6.163		104					300	1600; 1300				
			123			2.36		700	2200				
(b) Antiferromagnetic compounds													
Compound UX	a_0 (Å)	U-U (Å)	Type	T_N (°K)	n_a (μ_B)	χ (300°K) (10^{-6} cgs emu) χ_g χ_M	n_p (μ_B)	θ (°K)	T (°K)	ρ ($\mu\Omega$ cm)	R_H	γ (10^{-4} cal/ mole deg ²)	References
UN	4.8835	3.450	I	53±2	0.75	7.7	1960	3.0-3.1	-310	T_N 150-160			
	4.890							3.08 3.11±0.005		300 313; 182 160; 90	+	96	h, j, l, m, p, v, w, am
UP	5.5865	3.939	I	123	1.72±0.02	20.4	5487	3.31±0.02	+3	T_N 300	+		
	5.587			125	1.9			3.56	+36	300			j, l, m, x-z
	5.589			130						200; 244 (140-370)			n, ab-ab
UAs	5.766	4.068	I	128	1.89±0.05	19.2	6010	3.54	+32	300	238	+	j, ai-al
	5.771				2.13±0.05								
USb	6.1805	4.368	?	213	?	26.4	9500	3.85	+95	300	357	+	j, ai
	6.191												
UBi	6.364	4.490	?	290	?	16.5	7380	4.06	+115	?			aj

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- $U^{9+} (f^1)$, $U^{6+} (f^0)$. The sixfold ionized ion contains no unpaired electrons, and its compounds should be diamagnetic (apart from conduction-electron paramagnetism, if present); hence it cannot be present in the compounds discussed.
- The site symmetry is octahedral. Let
- $$\mathcal{H}_i = (\mathcal{H}_0 + \mathcal{H}')_i = (\mathcal{H}_0 + \mathcal{H}_e + \mathcal{H}_m)_i$$
- be the Hamiltonian of an ion i , where the $\mathcal{H}_0$ is the Hamiltonian of a free ion, $\mathcal{H}_e$ term is due to the electric field of the neighbors, and $\mathcal{H}_m$ describes the magnetic interaction. As we are concerned with the behavior of the ground multiplet only, we shall in future limit our discussion to the second and third perturbation terms. The crystal-field term of f -shell electrons in a cubic field depends on, the fourth- (O_4) and sixth-order (O_6) operators.⁷ The exchange interaction of the ion i with the surrounding ions can be written as arising from a Weiss magnetic field H_i . We assume, as is usual in the molecular-field theories of magnetism, that H_i is proportional to the average (sublattice) magnetization:
- $$\mathbf{H}_i = \sum_j \lambda_{ij} \mathbf{M}_j = \lambda \mathbf{M} = \lambda g \mu_B \langle \mathbf{J} \rangle, \quad (1)$$
- where g is the Landé factor and μ_B the Bohr magneton. The summation is over the j neighbors, and thus we obtain the Zeeman term $(\mathcal{H}_m)_i$ of the Hamiltonian of the i th ion
- $$(\mathcal{H}_m)_i = -\mathbf{u}_i \cdot \mathbf{H}_i = -(g \mu_B)^2 \langle \mathbf{J} \rangle \mathbf{J}_i \sum_j \lambda_{ij} = y W O_m. \quad (2)$$
- In the case of antiferromagnets discussed here, the absolute magnitude of magnetization of the different sublattices are equal. The field H_i is parallel to the easy direction of magnetization at the i th uranium-ion site. We now rewrite the Hamiltonian as function of the parameters x and y , expressing the relative magnitude⁸ of the local fields:
- $$\mathcal{H}_i' = W \{ [x O_4 / F(4) + (1 - |x|) O_6 / F(6)] (1 - y) - y O_m \}, \quad (3)$$
- where $F(4)$ and $F(6)$ are common factors taken from Steven's operator tables.⁷ Using this Hamiltonian one can calculate the energy eigenvalues and eigenfunctions (using as basis functions the eigenfunctions of J_z) for different values of x and y and orientations of H . Figure 1 shows as an example in the case of $J=4$, the dependence of the energy levels as well as the $\langle J_z \rangle$ on y for the case of $x=1$, and H parallel to the fourfold axis Oz . Such calculations for some other values of J have been performed by Ebina and Tsuya⁹ and on a more
- ⁷ M. T. Hutchings, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1965), Vol. 16; K. W. H. Stevens, *Proc. Phys. Soc. (London)* **A65**, 209 (1952).
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- ⁹ Y. Ebina and N. Tsuya, *Sci. Rept. Res. Inst. Tohoku Univ.* **12B**, 1 (1960); **12B**, 165 (1960); **12B**, 183 (1960); **13B**, 1 (1961); **13B**, 25 (1961); **13B**, 43 (1961); **15B**, 1 (1963); **15B**, 47 (1963); **15B**, 85 (1963).

TABLE II. Atomic parameters of some lanthanide and actinide ions.

f^n	Ion	Ionic parameters				Lowest excited multiplet		
		F_2 (cm ⁻¹) Slater-Condon	ξ (cm ⁻¹) Spin-orbit	Stevens (crystal)		Energy in cm ⁻¹		Ref.
				β	γ	Calc. by RS coupling	Expt.	
f^1	Ce ³⁺ 4f ¹		644			² F _{7/2}	2254	a
	Pa ⁴⁺ 5f ¹		1490	>0	0		5215	b
	U ⁵⁺ 5f ¹							
f^2	Pr ³⁺ 4f ²	305.4	729.5			³ H ₅	1823	c
	U ⁴⁺ 5f ²	206.1	1638	<0	>0		4095	d
f^3	Pr ²⁺ 4f ³	290.5	665			⁴ I _{11/2}	1219	e
	Nd ³⁺ 4f ³	332	906				1661	f
		327.5	884.6	<0	<0		1621	
	U ³⁺ 5f ³	196	1666				3054	g
f^4	Pm ³⁺ 4f ⁴	346	1070			⁵ I ₅	1338	h
	U ²⁺ 5f ⁴			>0	0			
	5f ³⁺ 6d ¹							
	Np ³⁺ 5f ⁴	225	2070				2588	i

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limited scale by Anderson and White¹⁰ (for $x = \pm 1$) and by Lea *et al.*⁸ for $y = 0$.

To compare the above calculation with experiments, we note that neutron diffraction data available so far have shown that, in the ordered state, the spins are aligned parallel to the fourfold axis. This we shall assume to be the case in all the compounds under discussion. Furthermore, from our own and other published results we see that the $\langle J_z \rangle$ and hence $\langle \mu_z \rangle$ of the ground level always increase with y . This consideration eliminates U³⁺, as the minimum magnetic moment of its possible ground states (at $y = 0$) is $1.33\mu_B$, and hence larger than the majority of the low-temperature

saturation magnetic moments in Table I. (These data were mainly obtained from magnetic measurements.) The published neutron diffraction data on the compounds UN,⁵ UP,⁵ and UAs,⁵ in the ordered state, were interpreted as indicating that uranium is probably in the U³⁺ state, but, as the authors themselves have stressed, they are not incompatible with the presence of U⁴⁺ compounds.

The approach, though not the details of the method employed here, is similar to that used by Bleaney¹¹ in his discussion of LnNi₂ compounds, where Ln denotes a rare earth.

The neutron diffraction studies so far show that in

TABLE III. Wave functions. Only major components larger than about 0.1 have been included in the table.

Configuration	Ion	Ground multiplet	g	Ref.
f^2 (³ H ₄)	U ⁴⁺	$0.874 ^3H_4\rangle - 0.331 ^1G_4\rangle - 0.214 ^3F_2\rangle - 0.195 ^3F_3\rangle + 0.138 ^3F_4\rangle + 0.097 ^3H_5\rangle$	0.824	a
f^3 (⁴ I _{9/2})	U ³⁺	$0.9128 ^3I_{20}\rangle - 0.3702 ^3H_{21}\rangle + 0.1214 ^3H_{11}\rangle$	0.739	b
	Nd ³⁺	$0.9847 ^3I_{20}\rangle - 0.1631 ^3H_{21}\rangle + 0.0566 ^3H_{11}\rangle + 0.0148 ^3G_{21}\rangle$	0.732	c
	Pr ²⁺	$0.9861 ^3I_{20}\rangle - 0.1560 ^3H_{21}\rangle + 0.0534 ^3H_{11}\rangle + 0.0151 ^3G_{21}\rangle$	0.732	d
f^4 (⁵ I ₄)	Np ³⁺	$0.8970 ^5I\rangle - 0.3045 ^4H_{30}\rangle + 0.1970 ^4H_{21}\rangle + 0.1918 ^3H_{11}\rangle$	0.6373	b

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¹⁰ R. L. White and J. P. Andelin, Phys. Rev. 115, 1435 (1959).

¹¹ B. Bleaney, Proc. Roy. Soc. (London) A276, 19 (1963); A276, 28 (1963).

the ordered state the moments are aligned parallel to O_z , one of the fourfold axes of the cube. In order to compare the theoretical predictions with experiment, we follow Trammell¹² and we write explicitly for the cubic crystal potential

$$\langle V_c \rangle = K_4(x^4 + y^4 + z^4 - 3/5) + K_6(11[x^6 + y^6 + z^6] - 15[x^4 + y^4 + z^4] + 30/7), \quad (4)$$

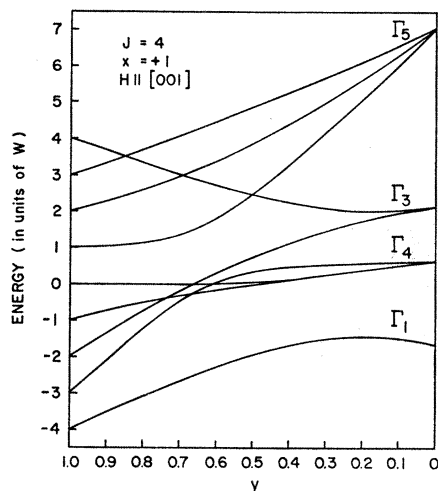
where

$$K_4 = \beta \mathcal{O}_4(J) 20 A_4 \langle r^{-4} \rangle$$

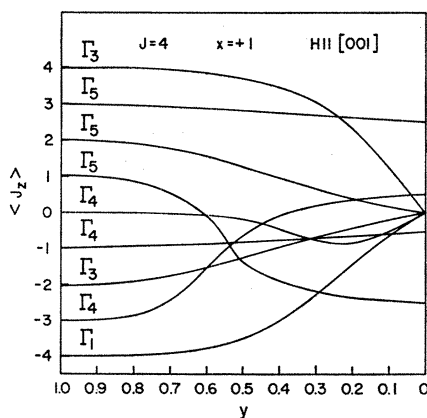
and

$$K_6 = \gamma \mathcal{O}_6(J) 56 A_6 \langle r^{-6} \rangle.$$

β and γ are Stevens' parameters, while $\mathcal{O}_i(J)$ are diagonal matrix elements $\langle J, J_z = J | \mathcal{O}_i | J, J_z = J \rangle$, taken from appropriate operator equivalent tables,⁷ and A_4 and A_6 are suitable sums over neighboring charges.⁸



(a)



(b)

FIG. 1. (a) Energy-level splitting for $J=4$, as function of the parameter y . (b) $\langle J_z \rangle$ for $J=4$, as function of the parameter y .

¹² G. T. Trammell, Phys. Rev. **131**, 932 (1962).

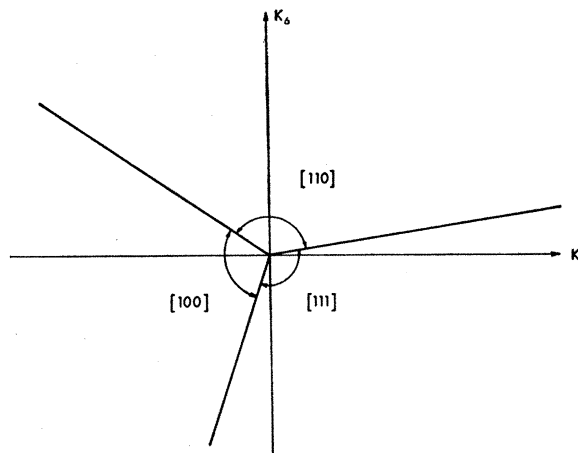


FIG. 2. Directions of energy minima as functions of the crystal-field parameters.

As shown by Trammell, if one considers semiclassically (for large J) the problem of dependence of energy on the orientation of the average momentum vector, the minima of $\langle V_c \rangle$ are the easy directions of magnetizations for the case of isotropic exchange interaction. These directions are shown graphically in Fig. 2 as functions of K_4 and K_6 .

The K_6/K_4 ratio is difficult to assess, for measurements on rare-earth compounds have shown that computations using hydrogenic or, even better, wave functions¹³ tend to underestimate K_6/K_4 severely. Inspection of Fig. 2 shows that the easy direction of magnetization, assuming $K_6/K_4 \ll 1$, is either $[100]$ for $K_4 < 0$, or $[111]$ for $K_4 > 0$. Inspection of Table II shows that only in the case of U^{3+} and U^{4+} is $\beta < 0$ and hence the easy direction of magnetization can be in the $[100]$ direction.

The accurate determination of the parameter x is a matter of some difficulty. As indicated above, computed wave functions are a rather unreliable guide. An alternative is to try to fit the magnetic susceptibility measurements, as carried out recently by Runciman and Rahman¹⁴ on U^{4+} in UO_2 . The comparatively wide discrepancies in susceptibility of UX , as reported in literature, probably due to poor composition control or impurities, do not seem to justify such an attempt at this stage. From rough calculations we expect x to be between 0.8 and 1; in more detailed calculations in this work we have limited ourselves to $x=1$.

It should be pointed out that in an octahedral field the ground state of U^{4+} in a purely electric field ($y=0$) is a singlet, and hence has no resulting moment; in the presence of an additional magnetic (exchange) field, the level becomes mixed with the higher level Γ_3 , which brings about the appearance of a moment.

¹³ R. E. Watson and A. J. Freeman, Phys. Rev. **127**, 2058 (1962).

¹⁴ R. U. Rahman and W. A. Runciman, J. Phys. Chem. Solids **27**, 1833 (1966).

TABLE IV. Lattice constants and ionic radii.
(a) UX compounds.

	UN	UP	Uv	Uv	Uv	Uv	Uvi	Uvi
			UAs	USb	UBi	US	USE	UTe
a (Å)	4.8835	5.5865	5.771	6.1805	6.364	5.4885	5.7435	6.157
r_{anion} (Å) ^a	1.48	1.86	1.91	2.08	2.13	1.82	1.93	2.11
$r_0 = \frac{1}{2}a - r_a$ (Å)	0.962	0.933	0.975	1.010	1.05	0.954	0.942	0.968
(b) Radii of uranium ions ^b								
U^{+n}	U ⁺¹	U ⁺²	U ⁺³	U ⁺⁴	U ⁺⁵	U ⁺⁶		
$r(U^{+n})$			1.03	0.93	0.89	0.83		

^a The anion radii taken from G. S. Zhdanov, *Fizika Tverdogo* (Tela M. G. U. Edit., Moscow 1961), pp. 184–185 [English transl.: *Crystal Physics* (Oliver & Boyd, London, 1965), pp. 192–193].

^b The uranium-ion radii in part (b) after the Zachariasen taken from C. Kittel, *Introduction to Solid State Physics* (John Wiley and Sons, Inc., New York, 1956), 2nd ed.

Table IV shows the lattice constants and conventional anionic radii of the compounds considered; also included are the radii of uranium ions in different ionization states.

The uranium radius calculated by subtracting the anion radius from the half of the crystal constant is remarkably constant and close to that obtained for U^{4+} in ionic compounds. This has already been pointed out by Allbut and co-workers¹⁵ for the case of Uvi compounds but also holds true for Uv compounds. The constancy of the uranium “ionic” radius so obtained agrees with the assumption that uranium appears in a fourfold ionized state in all these compounds, but of course it does not clinch the matter. It should be noted that the analogous Thv, Thvi compounds are diamagnetic, which indicates that they contain Th^{4+} ions, a state similar to that suggested for the Uv and Uvi compounds.

From the consideration of low-temperature magnetic saturation, direction of easy magnetization, ionic radii and later of susceptibility, one can draw the conclusion that the uranium is probably present as tetravalent ions. In future, our discussion will be mainly limited to this state.

IV. SATURATION MAGNETIZATION

We shall now consider in more detail the variation of saturation magnetization with temperature. The approach used will be a variation of the molecular-field theory, and we shall limit ourselves to the case of ferromagnets, the extension to antiferromagnets being quite straightforward. There are two relations between the magnetization M and the effective exchange field H_e .

The magnetization M is a function of the temperature T , the crystal-field intensity W , and the parameters x and y , introduced in Sec. III to describe the relative

intensity of the terms included in the Hamiltonian

$$M(y, x, W/kT) = \frac{\sum_{ij} \mu_{ij} \exp(-E_{ij}/kT)}{\sum_{ij} \exp(-E_{ij}/kT)}. \quad (5)$$

The levels are labeled by two subscripts. As the (electrostatic) crystal field is comparatively strong the conditions can be described by relatively small values of y , the levels are labeled by the subscript i to denote the representation (at $y=0$) they derive from and by subscript j to differentiate within the sublevels derived from a given i . There is also another relation between H and M : $H_i = \lambda M = ya/(1-y)g\mu_B$, where $a = (1-y)W$ is a measure of the crystal-field intensity. Hence

$$M = H_i/\lambda = yC/(1-y), \quad (6)$$

where C is initially unknown.

There are several methods of calculating the temperature variation of magnetization. Figure 3 shows one possible approach: From other sources of information we obtain the value of x that characterizes the material investigated (e.g., from susceptibility measurements). With this given x one computes the magnetization M as a function of W/kT for different values of the param-

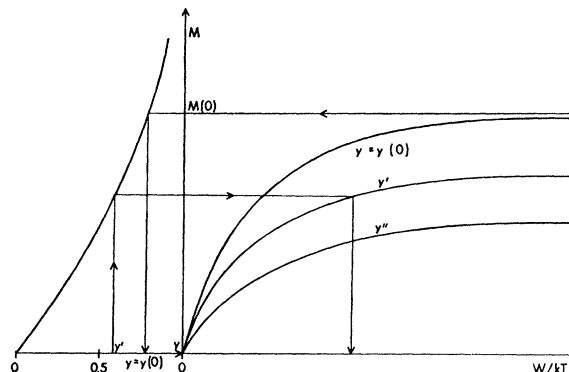


FIG. 3. $M(y, W/kT)$, saturation magnetization in the ordered state.

¹⁵ M. Allbut, A. R. Junkin, and R. M. Dell, in Proceedings of the International Symposium on Compounds of Interest in Nuclear Reactor Technology, Boulder, Colorado, 1965, pp. 65–81 (unpublished).

eter y . Such curves are plotted in the right part of Fig. 3. The saturation magnetization at 0°K determines $y(0^\circ\text{K})$ and hence the constant C , thus enabling us to use Eq. (6) to draw a curve $M=M(y)$ in the left part of Fig. 3. To determine M at temperatures different from zero, one proceeds as follows: Starting with a given value of y' on the left side of the graph, one obtains from the curve the corresponding value of M , and knowing y , selects the appropriate curve on the right half of the diagram, and thus obtains the value of W/kT . Hence one can plot a curve of $M(W/kT)$ as a function of T/T_c . From the experimental data on the Curie temperature T_c , one now determines W , the scale parameter of Fig. 1. We have employed a simplified version of this method which is quite satisfactory over the range of y that we were interested in. We expanded μ_{ij} and E_{ij} in Eq. (5) as series in powers of y . Retaining only the lowest nonzero terms it can be easily shown that the relation can be reduced to a form:

$$M(y, W/kT) = yQ(W/kT).$$

Now y can be eliminated between this relation and Eq. (6), giving $M=Q(W/kT)-C$. Again C is determined from the magnetization at 0°K. The master curve $Q=Q(W/kT)$ is plotted in Fig. 4, where the lines corresponding to the C 's of the different compounds are also drawn. The respective Curie (or Néel) temperatures were then used to calculate the crystal-field splitting, and the results are tabulated in Table V. The values are high compared with those obtained with lanthanide compounds, but compare reasonably with those obtained for other uranium compounds by entirely different methods. This splitting approaches the multiplet splitting, for the $J=5$ level is expected to be at about 5000 cm^{-1} . It is apparent that the approximations used approach the limit of their applicability.

V. SUSCEPTIBILITY

The magnetic susceptibility of a gram molecule of paramagnetic ions is given by the Van Vleck theory, as

$$\chi_M = N_A \frac{\sum_{n,m} [(E_{n,m}^{(1)})^2/k_B T - 2E_{n,m}^{(2)}] \exp(-E_{n,m}^{(0)}/k_B T)}{\sum_{n,m} \exp(-E_{n,m}^{(0)}/k_B T)}, \quad (7)$$

where the coefficients are the terms of the series used to express the energy of a given ion level as polynomial in

TABLE V. Total crystal-field splitting (cm^{-1}) of the ground multiplet $J=4$.

Compound	UN	UP	US	USe	UTe
$E(\Gamma_6) - E(\Gamma_1)$ $\approx 8.6W$	500	720	1150	1100-1400	750-880

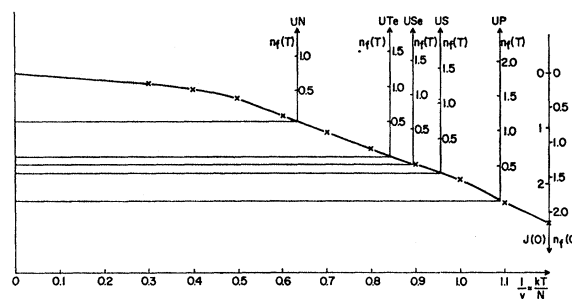


FIG. 4. Saturation magnetization in the ordered state.

H , the applied magnetic field

$$E_{n,m} = E_n^0 + H E_{n,m}^{(1)} + H^2 E_{n,m}^{(2)},$$

where n, m are quantum numbers, and N_A is Avogadro's number. This is applicable at temperatures well above the Curie (or Néel) point of the compound and also sufficiently high in comparison with the crystal-field splitting of the ions (but still small in comparison with the energy of the next higher multiplet). This must be corrected for the presence of the exchange interaction. This interaction can be approximated as before by means of the average Weiss field theory (that is, by assuming as before that the exchange interaction of site i is proportional to the average polarization) ($H_i = \lambda M$), hence

$$\chi(T) = \chi^0(T) / [1 - \lambda \chi^0(T)], \quad (8)$$

where $\chi^0(T)$ is the susceptibility as given by Eq. (7) and λ is the appropriate proportionality constant.

Hence, at high temperatures the slope of the $1/\chi$ versus T graph should be equal to that of $1/\chi^0$, which in turn is given by $(N n_p^2 \mu_B^2 / 3 k_B)^{-1}$, where $n_p^2 = g^2 J(J+1)$, g is the Landé constant, J is the J -quantum number of the ground multiplet of the ion, and n_p is the number of Bohr (paramagnetic) magnetons. In Fig. 5 we have plotted the computed values of n_p and of $1/\chi T$ as function of $k_B T/W$, where W is the crystal-field splitting parameter, in the case of U^{4+} and $x=1$. Similar graphs have been prepared also for the U^{3+} ($^4I_{9/2}$) configuration. At low temperatures there are strong departures, but at temperatures sufficiently high above the Curie (Néel) temperature the value of n_p (that is, the slope of the reciprocal of the susceptibility versus temperature) becomes constant. The experimental values of n_p of the Uv compounds agree with those calculated for U^{3+} and U^{4+} , while those of Uvi compounds are much lower, approximating to those calculated for U^{5+} . This is possibly due to the contribution of the polarization $P(r)$ of the conduction electrons. Integrating over all space and assuming RKKY coupling, one obtains the contribution to the magnetic moment per cation^{16,17}:

$$\Delta M = 2\mu_B \int P(r) d^3r = \frac{3}{4} \mu_B Z \Gamma (g-1) J / E_F. \quad (9)$$

¹⁶ S. H. Liu, Phys. Rev. **123**, 470 (1961).

¹⁷ P. G. de Gennes, J. Phys. Radium **23**, 517 (1962).

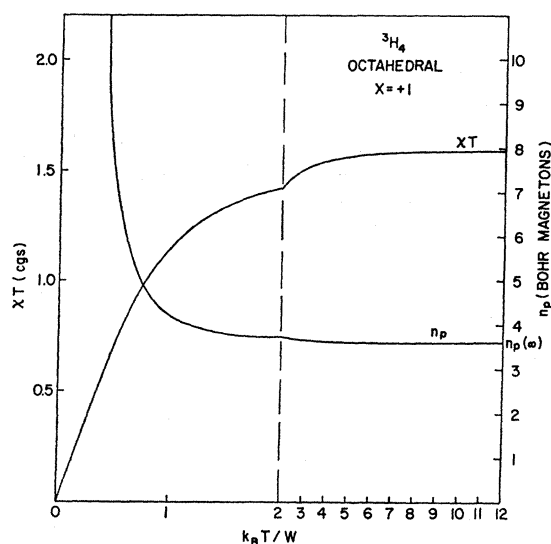


FIG. 5. Magnetic susceptibility and n_p as functions of temperature for $J=4$.

For example, in gadolinium the experimental value of n_p is about 0.5 lower than calculated, which is probably due to this effect. However, it is doubtful whether the appreciable discrepancy in n_p observed in Uvi compounds can be explained on this basis. Another possible contributing factor may be due to the very strong electron coupling between anions and cations. This brings about partial transfer of electrons to the cation and gives rise to a partially covalent bond as observed in some transition-metal compounds.¹⁸ However, this contradicts our initial assumption that the 5f electrons are concentrated on the cations and well screened. Though useful as a zero approximation, this assumption is not entirely correct, and this must be taken into consideration, not only in the case of 5f but even in that of 4f electrons, which have a much smaller radius.¹⁹ Both these effects should also manifest themselves by a lowering of the saturation magnetization in the ordered state.

VI. ELECTRON BAND STRUCTURE

Assuming that the uranium atoms are fourfold ionized, the distribution of electrons among the different bands is shown in Fig. 6. We assume that the band structure is schematically as shown therein, where the band np of the anion is filled by adding two electrons in the case of Uvi, or three electrons in the case of Uv. The 5f narrow band or rather localized states contain 2 electrons, while the $7s/6d$ conduction band contains one or two electrons, respectively. The suggested energy band scheme resembles that proposed for

metallic uranium by Rocher and Friedel,²⁰ except that because of the increased distance between uranium ions, the 5f sub-band has narrowed and separated below the conduction band, which now derives only from the 7s and 6d levels. The proposed band structure agrees with the high electric conductivity reported for these compounds (Table I).

The published data on Hall-effect measurements show comparatively high positive coefficients, hence seemingly indicating conduction by holes and low concentration of carriers. As the materials are magnetic, one cannot apply the elementary theory of the Hall effect (as in the case of many semiconductors), for the theory of the ordinary and extraordinary Hall effects in ferro- and antiferromagnetic materials is notoriously complicated. Hence, one cannot draw any direct conclusions from the Hall-effect measurements as to the band structure and carrier concentration.

The reported values for the thermoelectric coefficients are low and positive, indicating a reasonably high concentration of carriers. The available electron specific-heat data are extremely high (among the highest reported in literature), in apparent disagreement with the Hall-effect measurements.

VII. RKKY INTERACTION

The interaction between a single 5f electron localized at R_n , and a wave function $\Psi(r-R_n)$, may cause scattering of a conduction electron from an occupied state k to a vacant one k' .^{2,21} Hence spin on atom n sets up a spin polarization of conduction electrons in the vicinity. In second order of perturbations this brings about a coupling between spins of neighboring atoms, a coupling with a fairly long range. The second-order change in energy, due to this interaction between spins

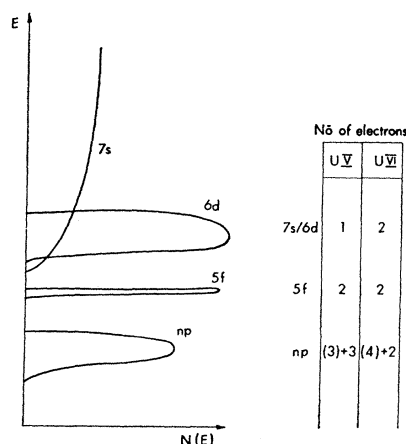


FIG. 6. Energy bands.

¹⁸ J. Owen and J. H. M. Thornley, Rept. Progr. Phys. **29**, 675 (1966).

¹⁹ See Ref. 6, pp. 217-219 and the references quoted there, especially J. C. Eisenstein, J. Chem. Phys. **25**, 142 (1956); C. K. Jorgensen, Phys. Status Solidi **2**, 1146 (1962).

²⁰ Y. D. Rocher and J. Friedel, J. Phys. Chem. Solids **21**, 287 (1961).

²¹ M. A. Ruderman and C. Kittel, Phys. Rev. **96**, 99 (1954); K. Yosida, Phys. Rev. **106**, 893 (1957); T. Kasuya, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1966), Vol. IIB.

$\mathbf{S}_m$ and $\mathbf{S}_n$, is given by

$$\begin{aligned}
 E_M(m, n) &= (2G^2/N^2) \sum_{|k| \leq k_F} \sum_{|k'| > k_F} \\
 &\times \{ \exp[i\mathbf{q}(\mathbf{R}_n - \mathbf{R}_m)] \mathbf{S}_n \cdot \mathbf{S}_m / [E(k') - E(k)] \} \\
 &= \int_{-k_F}^{k_F} k dk \int_{-\infty}^{\infty} k' dk' \frac{\exp i\mathbf{q} \cdot \mathbf{R}_{nm}}{E(k') - E(k)} \\
 &= (\pi \Gamma^2 \mathbf{S}_m \cdot \mathbf{S}_n m^* / 6\hbar^2) k_F^4 F(2k_F R_{nm}) \\
 &= 9Z^2 \Gamma^2 \mathbf{S}_n \cdot \mathbf{S}_m F(2k_F R_{nm}) / 4V^2 E_F, \quad (10)
 \end{aligned}$$

where G is similar to atomic $6d$ - $5f$ and $7s$ - $5f$ exchange integrals, and probably does not depend strongly on k and k' .

The Rudermann-Kittel function is given by $F(x) = (x \cos x - \sin x)/x^4$, where $\mathbf{q} = \mathbf{k} - \mathbf{k}'$, E_F is the Fermi energy, V is the atomic (ionic) volume, Z is the number of conduction electrons per cation, and the energy spectrum has been approximated by that of free electrons $E(k) = \hbar^2 k^2 / 2m^*$. Although formally the equation was obtained by integrating k' between $-\infty$ and $+\infty$, and k between $-k_F$ and k_F , the actual contribution is only from states very close to the Fermi surface, since contributions from farther away vanish. Hence the assumptions used in derivation of Eq. (10) do imply a parabolic energy band only within $E_F \pm \epsilon$ ($\epsilon/E_F \ll 1$), and not over all the energy range, as is apparently implied. Hence, derivation of Eq. (10) does not require the assumption of a whole, quasifree electron parabolic band, which in our case is unlikely.

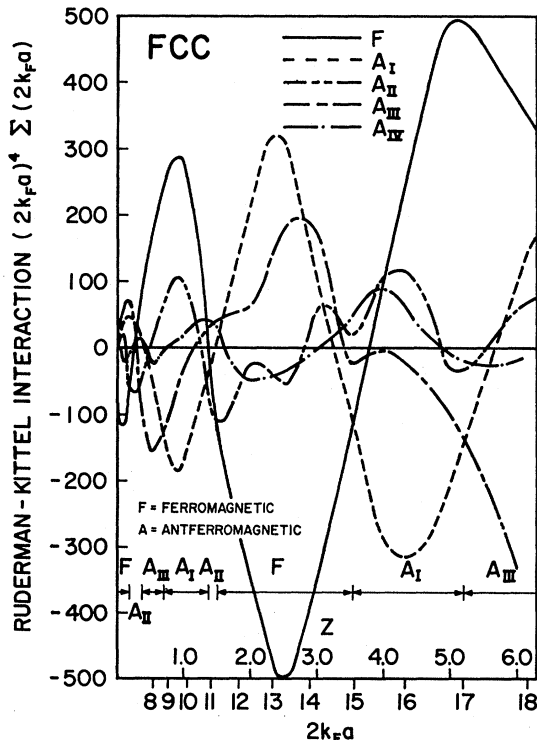


FIG. 7. RKKY sums in fcc lattices and regions of stability of magnetic order.

If G does depend on $\mathbf{k}$ and $\mathbf{k}'$, this can be taken into account, and though the expression becomes complicated, the long-range oscillatory character of Eq. (10) is preserved (Ref. 2, p.408).

As we assume that for electrons in the $5f$ state J is a constant of motion, S should be replaced by $(g-1)J$.

The electron spin interaction energy is given by summation of $E_M(n, m)$ over all ion pairs:

$$\begin{aligned}
 E_M &= 9\pi Z^2 G^2 (4V^2 E_F)^{-1} (g-1)^2 J(J+1) \sum_{n \neq 0} F(2k_F R_{0n}) \\
 &= m^* \Gamma^2 (g-1)^2 J(J+1) (32\pi^3 \hbar^2 a^4)^{-1} P(2k_F a), \quad (11)
 \end{aligned}$$

where the sum is taken over the paramagnetic ions and $P(2k_F a) = (2k_F a)^4 \sum_{n \neq 0} F(2k_F R_{0n})$. It is doubtful to what extent such a simplified model will correspond to actual materials. Further refinements of the simple RKKY theory, in order to take into account more complicated band form, dependence of G on $\mathbf{q}$, anisotropy, and so on, have been discussed in the literature.^{2,22-25} Such models have been initially applied to lanthanide metals² and more recently to some of their compounds.^{3,25-27}

Figure 7 shows the dependence of the RKKY interaction term as function of $(2k_F a)$ or Z —the number of free charge carriers per cation for the rock-salt fcc lattice and for the cases of ferro- and antiferromagnetic ordering. We have not included in our calculations the effect of electron scattering, which reduces the range of interactions, as proposed by de Gennes.¹⁷ For the ferromagnetic case only, similar calculations have been published by Mattis^{28,29} and by Methfessel.³

By inspection of the graph one can determine which structure has the minimum energy (at given value of $2k_F a$) and hence is the stable structure (at low temperature).

We find from Fig. 7 that for $Z=2$, using for Z the numbers listed in Fig. 6 (which we identify with Uvi compounds), the state with the lower energy is ferromagnetic, while for $Z=1$ (Uv compounds) it is antiferromagnetic of type-I order, in agreement with the neutron diffraction measurements on UN, UP, and UAs. The curve for the ferromagnetic order is proportional to θ , the paramagnetic Curie temperature. Inserting reasonable values, namely $\theta = 200^\circ \text{K}$, $a = 5.4 \text{ \AA}$, $J = 4$, $g = \frac{4}{5}$, $R(2k_F a) = -500$, we obtain for $\Gamma^2 m^* / m = 840 \text{ (eV \AA}^3)^2$, which can be interpreted as

²² K. Yosida and A. Watanabe, Progr. Theoret. Phys. (Kyoto) **28**, 361 (1962).

²³ R. J. Elliott and F. A. Wedgwood, Proc. Phys. Soc. (London) **81**, 846 (1963); **84**, 63 (1966).

²⁴ T. Kasuya and D. H. Lyons, J. Phys. Soc. Japan **21**, 287 (1966).

²⁵ A. J. Freeman and R. E. Watson, Phys. Rev. **152**, 566 (1966).

²⁶ F. Holtzberg, T. R. McGuire, S. Methfessel, and J. C. Suits, J. Appl. Phys. **35**, 1033 (1964).

²⁷ (a) Y. A. Rocher, Advan. Phys. **11**, 233 (1962); (b) M. I. Darby and K. N. R. Taylor, Phys. Letters **14**, 179 (1965); (c) R. Lallemand, thesis, University of Paris, 1966, Report CEA, R. 3043 (unpublished).

²⁸ D. Mattis and W. E. Donath, Phys. Rev. **128**, 1618 (1962).

²⁹ D. Mattis, N. Anthony, and L. Horowitz, IBM Report RC 945, 1963 (unpublished).

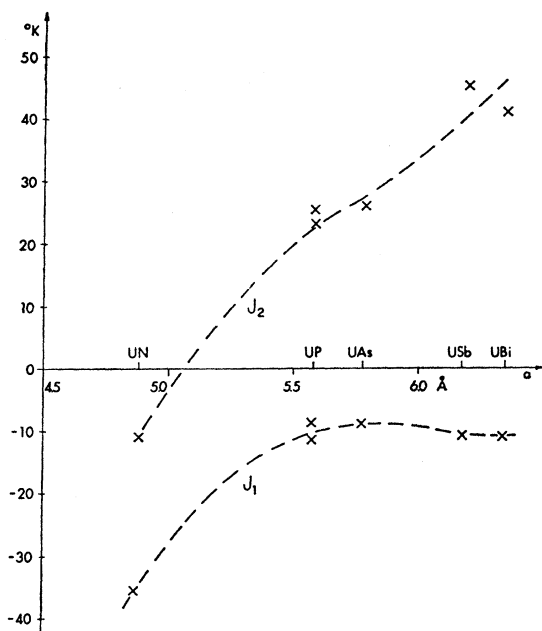


FIG. 8. The exchange interaction constants J_1 , J_2 in UX compounds as a function of lattice constant.

$m^*/m=3$, and $\Gamma=17.6 \text{ eV } \text{\AA}^3$, both reasonable values though large.

However, according to the theory, the paramagnetic Curie temperature θ of the compounds of a given group should be proportional to (m^*a^{-4}) , assuming that other parameters do not vary significantly. This is not the case, nor does there seem to be a simple relation between θ and the lattice spacing a . What is more, the Curie temperature of UN is negative, while that of other Uv compounds is positive, and the problem of the change of sign of θ seems rather difficult to account for. One can try to analyze the experimental results by using the molecular-field theory³⁰ of compounds with the nearest-neighbor interaction (J_1) and the next nearest (J_2), and calculate J_1 and J_2 interaction constants from the experimental values of the paramagnetic Curie temperature and the Néel temperature (Table I).

The reported ratio of θ/T_N for UN cannot be explained by the theory (due to the neglect of long-range interaction present in UN). Even a slightly reduced θ/T_N would demand the second or third type anti-ferromagnetic ordering, and not the first type as observed. If we now postulate that, apart from the RKKY mechanism, there is an additional exchange coupling via the intervening anions, one could write

$$J_i = J_i(\text{RKKY}) + J_i(\text{se}), \quad i=1, 2$$

where the first term is due to the RKKY interaction while the second is due to a superexchange mechanism. One would then expect J_i to be large for small a , then

³⁰ J. S. Smart, *Effective Field Theories of Magnetism* (W. B. Saunders, Philadelphia, 1966).

decrease rapidly and become constant for large a , at the value determined by the interaction constant J_i (RKKY) only. This is approximately so in the case of J_1 (Fig. 8), but J_2 changes sign and does not level out for large a , as expected above. J_2 depends on interaction among three ions arranged in a straight line (angle 180°), as compared with J_1 , which acts through a 90° angle, and it is possible that the former is of longer range than the latter.

Also, the variation of θ (and of T_c) of the ferromagnets of the Uvi group is difficult to explain satisfactorily within the framework of our assumption.

We have however neglected several, possibly important, effects. Firstly, the range of the RKKY interaction may be limited, and thus may have a most definite effect on θ .^{27c,31} Secondly, it is quite possible that, due to changes of the electron potential field on passing from one compound to the other, there is an appreciable distortion of the Fermi surface, and hence a change in the average value of $(2k_F a)$. Such an explanation was already suggested in the case of compounds of group VA and VIA elements with rare earths with Th_3P_4 structure.²⁶

VIII. ELECTRICAL PROPERTIES

The available data are rather meager and are included in Table I. It is clear that the room-temperature resistivity is very low, of the order of $200 \mu\Omega \text{ cm}$, about an order of magnitude larger than that of metallic uranium ($\sim 30 \mu\Omega \text{ cm}$).

The only available extensive data on the temperature variation of resistivity in the neighborhood of the magnetic transition temperature are those on USe ,³² UP , US ,³³ and UN .³⁴ They all show a steep rise of resistivity with the temperature up to the transition point, where a sudden change of slope takes place. This is very similar to the behavior of some of the lanthanide metals, where it has been explained as due to the increased scattering of the conduction electrons by the lattice of the localized magnetic moments. This lattice becomes more disordered as the temperature rises towards the Curie (or Néel) point, since the number of reversed moments increases.^{35,36}

The theory gives the maximum contribution to resistivity (at the magnetic transition temperature), due to this cause, as

$$\rho_m = (3\pi N m / 8 \hbar e^2 E_F) \Gamma^2 (g-1)^2 J(J+1).$$

³¹ P. G. de Gennes, *J. Phys. Radium* **23**, 630 (1962).

³² L. K. Matson, J. W. Moody, and R. C. Himes, *J. Inorg. Nucl. Chem.* **25**, 795 (1963).

³³ C. W. Kazmierowicz, Argonne National Laboratory Report No. ANL-6731, 1963 (unpublished); M. A. Kanter and C. W. Kazmierowicz, *Bull. Am. Phys. Soc.* **9**, 633 (1964).

³⁴ P. Costa, R. Lellement, F. Anselin, and D. Rossignol, in *Proceedings of the International Symposium on Compounds of Interest in Nuclear Reactor Technology*, Boulder, Colorado, 1965, pp. 83-91 (unpublished).

³⁵ P. G. de Gennes and J. Friedel, *J. Phys. Chem. Solids* **4**, 71 (1958).

³⁶ A. J. Dekker, *J. Appl. Phys.* **36**, 906 (1965).

ρ_m is usually obtained by back-extrapolation to $T=0^\circ\text{K}$ of the high-temperature (above T_c or T_N) part of the resistivity curve, to eliminate the additional contribution due to phonon scattering. As except for UN, USe, and US, we have not been able to find sufficiently complete data on the temperature variation of the resistivity, we shall use $\rho(T_c)$ in place of ρ_m , which overestimates ρ_m slightly. Now measurements of θ and of ρ_m enable us to calculate Γ and m^*/m for the different compounds. The results are shown in Fig. 9, which also includes several related materials. The range of values obtained is

$$\Gamma = 12\text{--}22 \text{ eV } \text{\AA}^3, \quad m^*/m = 3\text{--}9,$$

which seems to be reasonable. Most of the electric resistivity data have been obtained on sintered specimens, and probably represent only an upper limit. The influence of purity has also not been investigated but it is to be expected that careful purification would only reduce ρ_m as in metals. This is probably the case with UTe, where a lower ρ_m would give more reasonable values of Γ and of m^*/m .

In the lanthanides, the calculated Γ is about four times smaller than in the uranium compounds. This agrees with conclusions of Jaccarino and his co-workers,

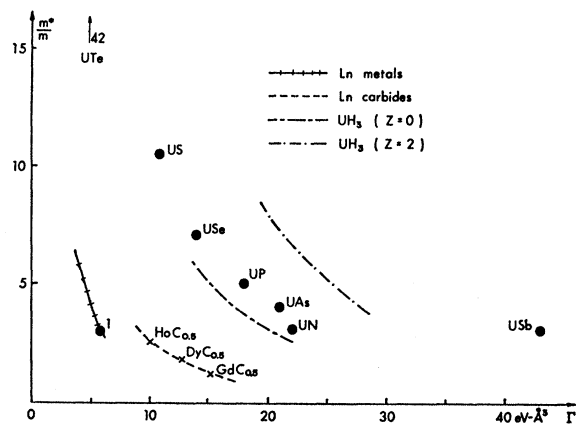


FIG. 9. The effective electron mass m^* and coupling constant Γ in UX and some related compounds. Ln denotes lanthanides. Point 1 is taken from Y. Rocher, Ref. 27a; the data on Ln carbides from R. Lallemand, Ref. 27c; the two curves for UH_3 were calculated using two different assumptions concerning the number of conduction electrons.

who, using a slightly different formulation, determined the f - s coupling from measurements of the Knight shift of aluminium in UAl_2 ³⁷ and in the analogous aluminium-rare-earth alloys, as well as from Δg in ESR.³⁸

IX. DISCUSSION

The proposed model seems reasonably successful in accounting for some of the properties of the uranium compounds, in spite of being obviously primitive. It is no more than a crude first approximation of the actual state of affairs. It is similar to models proposed for metallic lanthanides and some of their compounds.

As is to be expected, such a model based on the assumption of strongly localized magnetic electrons would be more appropriate in the case of $4f$ than $5f$ electrons, for it is well known that the radius of the latter is larger than that of the former. For this reason one would expect strong overlap with the neighboring atoms, and the possibility of bonds arising from $5f$ shell electrons. According to the above model, one of the important differences between uranium and the lanthanides is the fact that rare-earth ions usually appear as triply ionized, while uranium is more variable in its valency, and, for example, in the cases considered above, was assumed to be tetravalent. The comparison of uranium compounds with those of its lanthanide analog neodymium shows that, as expected, NdS, NdSe, and NdTe are antiferromagnetic; while of the NdV compounds, NdN and NdP are ferromagnetic,³⁹ as expected on the basis of our model (assuming that neodymium appears as Nd^{3+}). However, the fact that NdAs and NdSb are antiferromagnetic³⁹ cannot be accounted for on the basis of the simple model, without additional assumptions.

As in the lanthanides Γ is about four times less than in the uranium compounds, the RKKY coupling there is much weaker and other mechanisms might easily become important in the lanthanides and their compounds.

³⁷ A. C. Gossard, V. Jaccarino, and J. H. Wernick, Phys. Rev. **128**, 1038 (1962).

³⁸ V. Jaccarino, B. T. Matthias, M. Peter, H. Suhl, and J. H. Wernick, Phys. Rev. Letters **5**, 251 (1960); D. Shaltiel, J. H. Wernick, H. J. Williams, and M. Peter, Phys. Rev. **135**, A1346 (1964).

³⁹ G. Busch, J. Appl. Phys. **38**, 1386 (1967).