

# Magnetism of actinides and their compounds

K. G. Gurtovoi and R. Z. Levitin

*I. V. Kurchatov Institute of Atomic Energy, Moscow*

*M. V. Lomonosov State University, Moscow*

*Usp. Fiz. Nauk* **153**, 193–232 (October 1987)

A review of the current status of theoretical and experimental investigations of the magnetism of actinides and their compounds is given. The electron structure of actinides is considered and information is given on the magnetism of actinide metals. The problem of the actinide valence in compounds (specifically, the phenomenon of mixed valence) is analyzed. A review is given of the models which allow for the collectivization of the 5f electrons and for their hybridization with other groups of electrons in actinide compounds. Variation of the magnetic properties with the degree of collectivization is studied. Descriptions are given of the characteristics of the critical behavior and of magnetic excitations in actinide compounds. Data are provided on the magnetic anisotropy and on magnetoelastic interaction in actinide compounds.

## CONTENTS

1. Introduction.....	827
2. Electron structure of actinides .....	828
3. Magnetic properties of actinides .....	830
4. Valence of actinides in compounds .....	833
5. Magnetic properties of actinide compounds. Hill diagram .....	834
6. Compounds with band magnetism .....	836
7. Magnetic properties of compounds with almost-localized 5f electrons.....	838
8. Characteristics of critical behavior and magnetic excitations in actinide compounds.....	844
9. Magnetic anisotropy and magnetoelastic effects .....	845
10. Conclusions.....	848
References.....	848

## 1. INTRODUCTION

In 1952 an outstanding Polish scientist W. Trzebiatowski and his colleagues discovered<sup>1</sup> that uranium trihydride  $\beta$ -UH<sub>3</sub> becomes ferromagnetic below 173 K. This was an experimental proof that, in addition to elements in the iron group and rare earths, there is a third group of elements (actinides) whose compounds exhibit a "strong" magnetism and it provided a stimulus for investigations of magnetic ordering in actinides. In subsequent years the rate of growth of research on the magnetism on actinide compounds has been accelerating in many laboratories throughout the world and at present several hundreds of different ferromagnetic, ferrimagnetic, and antiferromagnetic compounds of uranium, neptunium, plutonium, americium, etc., are known.

However, in spite of the major progress in experimental studies, the nature of the magnetism of actinide compounds has not yet been investigated sufficiently thoroughly: we know much less about these compounds than about the nature of magnetism of rare-earth compounds, the study of which started not much earlier than those of actinides. In our view, this is due to at least two factors.

Firstly (and this is the main factor), the magnetism of actinides (and particularly of the first half of the group up to curium) has a much more complex origin than the magnetism of rare earths. In most cases in the former case we cannot use the simple models employed successfully in accounting for the magnetic properties of the majority of rare-earth compounds.

Secondly, whereas experimental studies of rare earths have covered the full range (apart from promethium) between lanthanum and lutetium and their compounds, which makes it possible to obtain important information on the nature of their magnetism by comparing the magnetic properties of different rare earths, in the case of the actinide series only thorium and uranium have been readily available to most investigators and serious experimental difficulties have been encountered in the study of transuranium elements because of their high radioactivity and a short half-life. Systematic investigations of the magnetism of transuranium compounds have begun only recently and they have been carried out in the laboratories of nuclear research centers in various countries. It has been necessary to work with small (of the order of a microgram) amounts of a substance under strong radiation conditions, to allow for the change in the composition of a sample with time because of radioactive decay, and to take account of the effects due to formation of radiation defects, radiation self-heating, etc. All these difficulties reduce the precision of the experiments and the reliability of the results.

Several reviews<sup>2-4</sup> and monographs<sup>5-7</sup> published abroad have dealt with the experimental data on the magnetism of actinides and with the theoretical interpretations. In the Soviet literature we found only one short review paper dealing mainly with the electron structure of actinides.<sup>8</sup> The present review intends to fill this gap at least partially. Our task was not to write a handbook summarizing all the published information on magnetic actinide compounds. Our

main aim was to demonstrate (using the most striking examples) the current status of the experimental studies of magnetic properties of actinides, to present the current ideas on the nature and characteristics of their magnetism, and to compare the theoretical models of the magnetism of actinides with the models describing the magnetism of the much more thoroughly investigated transition 3d and rare-earth 4f magnetic materials. In the selection of the cited papers we gave preference, whenever possible, to those which provided an overall view of the results obtained on specific topics discussed below.

## 2. ELECTRON STRUCTURE OF ACTINIDES

Actinides is the name given to a family of elements in the seventh period of the Mendeleev table located beyond actinium. This family consists of 15 elements with the atomic numbers 89–103.

Actinides are transition elements in which one of the inner electron shells in an atom is only partly filled. In the case of actinides it is the 5f shell. The electron structure of actinide atoms is given in Table I. It is clear from this table that the partly filled 5f shell of actinides is screened by the 6s and 6p shells, above which there are the valence 6d and 7s electrons.

The reason for the existence of inner partly filled shells in many-electron atoms is that the energy of an electron in an atom depends not only on the principal quantum number  $n$ , but also on the orbital quantum number  $L$ . For a given value of  $n$  the energy increases on increase in  $L$  at a rate which becomes greater on increase in the difference between the strong self-consistent field of a many-electron atom and the Coulomb field of a hydrogen-like atom. Therefore, the energy considerations may favor an increase not in the orbital quantum number  $L$  (for a constant  $n$ ), but in the principal quantum number  $n$  of an electron which is added on transition to the next element.

There is a certain analogy between actinides and rare earths in which the 4f shell is partly filled (Table I). However, there are also certain differences in the occupancy of the f shells in atoms of these two groups of elements. In the case of rare earths the occupancy is more consecutive: an increase in the atomic number by one in most cases increases by unity also the number of electrons in the 4f shell ("discre-

pancies" are observed only in three cases: on transition from cerium to praseodymium, from europium to gadolinium, and from gadolinium to terbium). In actinide atoms the 5f shell does not fill up in an equally regular manner. In the case of actinides the "discrepancies" occur in five cases (on transition from actinium to thorium, from thorium to protactinium, from uranium to neptunium, from americium to curium, and from berkelium to californium). This is due to the fact that, as demonstrated in the calculations in Ref. 9, the configurations of an atom with different numbers of the f electrons (and, consequently, of the d electrons) in the case of actinides differ less in respect of the energy than in the case of rare earths.

Magnetic and other physical properties of transition metals and, in particular, of actinides depend on the degree of collectivization of electrons of partly filled inner shells in a solid, which can be regarded as depending mainly on the ratio of the radius of the partly filled shell to the distance between the nearest atoms. The 5f shell of an actinide atom (average radius 0.7 Å) is more extended than the partly filled 4f shell of a rare-earth atom (average radius 0.5 Å), but it is smaller than the partly filled 3d shell of a transition-element atom belonging to the iron group (average radius 0.8–0.9 Å).<sup>10</sup> The dimensions of partly filled shells in atoms of the 4d and 5d transition elements are even greater. Therefore, actinides occupy an intermediate position between rare earths, the majority of the properties of which can be described satisfactorily by the model of localized 4f electrons, and transition metals belonging to the iron group, in which case the effects due to collectivization of the 3d electrons are important. We must also allow for the fact that because of the actinide compression effect the size of the 5f shell decreases on increase in the atomic number, so that we can expect an increase in the degree of localization of the 5f electrons as we go over from actinium to lawrencium in the actinide series.

The change in the ratio of the calculated radius of the 5f shell ( $r_{5f}$ ) to half the distance between the nearest atoms  $R = d_{An}/2$  in metallic actinides is demonstrated in Fig. 1 (which is based on the data taken from Ref. 11). We can see that for metals lying to the left of americium (excluding thorium) this ratio is greater than for iron. Therefore, in the case of light actinides the 5f electrons are in the collective

TABLE I. Shells of actinide and lanthanide atoms additional to filled (radon- and xenon-like) shells.

	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
7s	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
6d	1	2	1	1	—	—	—	1	1	—	—	—	—	—	1
6p	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6
6s	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
5f	—	—	2	3	5	6	7	7	8	10	11	12	13	14	14
	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
6s	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
5d	1	1	—	—	—	—	—	1	—	—	—	—	—	—	1
5p	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6
5s	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
4f	—	1	3	4	5	6	7	7	9	10	11	12	13	14	14

state and these metals resemble more closely the 3d elements than do rare earths. Only beginning from americium can we regard the 5f electrons as localized, although even then we have to allow for the hybridization of the 5f, 6d, and 7s states.

A change in the degree of collectivization of the 5f electrons results in a nonmonotonic dependence of the properties along the actinide series. Figure 2 gives the molar volumes<sup>12</sup> of actinides, lanthanides, and 3d, 4d, and 5d transition metals. We can see that in the case of light actinides the molar volumes are closer to the volumes of the d transition metals than to the molar volumes of rare earths and, as in the case of the d transition metals, actinides exhibit a parabolic dependence of the molecular volume on the atomic number. Only beginning from americium do the molar volumes of actinides become close to the molar volumes of rare earths. Such a nonmonotonic dependence of the molar volume of actinides on the atomic number is due to the participation of the collective-state (itinerant) 5f electrons of light actinides (Th, Pa, U, Np, Pu) in the metallic binding.

These observations and other experimental data were analyzed in a systematic manner by Smith and Kmetko,<sup>13</sup> who constructed an empirical periodic table of transition metals (Fig. 2b). According to this table, the degree of localization of electrons in the partly filled shells of transition metals increases as we move to the right along the rows or up along the columns. Electrons in the partly filled shells of the metals which are to the left of the shaded region can be regarded as collectivized, whereas those on the right can be thought of as localized. The shaded region represents those metals in which the d or f electrons are in an intermediate state. The electron structure of such metals is very unstable, so that these metals are characterized by lower melting points and a large number of allotropic transitions (for example, plutonium exhibits six different crystalline modifications).<sup>14</sup> The phase diagrams of alloys of the metals in the shaded region are very complex. The phase diagrams of U-Np and Np-Pu alloys are more complicated than the phase diagrams of other binary systems of light actinides.<sup>13,14</sup> The instability of the electron structure accounts also for the high catalytic activity and the ability of such systems to absorb considerable amounts of hydrogen.<sup>14</sup>

This sharp division of actinide metals into two groups with collectivized (itinerant) and localized 5f electrons is

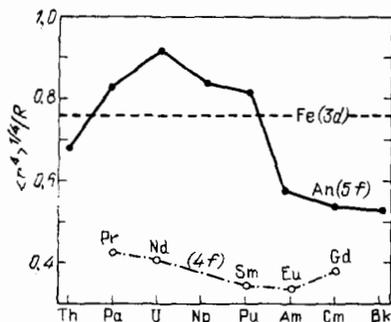


FIG. 1. Ratio of the average radius  $\langle r \rangle$  of the 5f shell to half the actinide-actinide distance  $R = d_{An}/2$  in the  $\alpha$  modifications (double hexagonal crystal structure) of metallic actinides.<sup>11</sup> The corresponding data for rare earths and iron are also included.

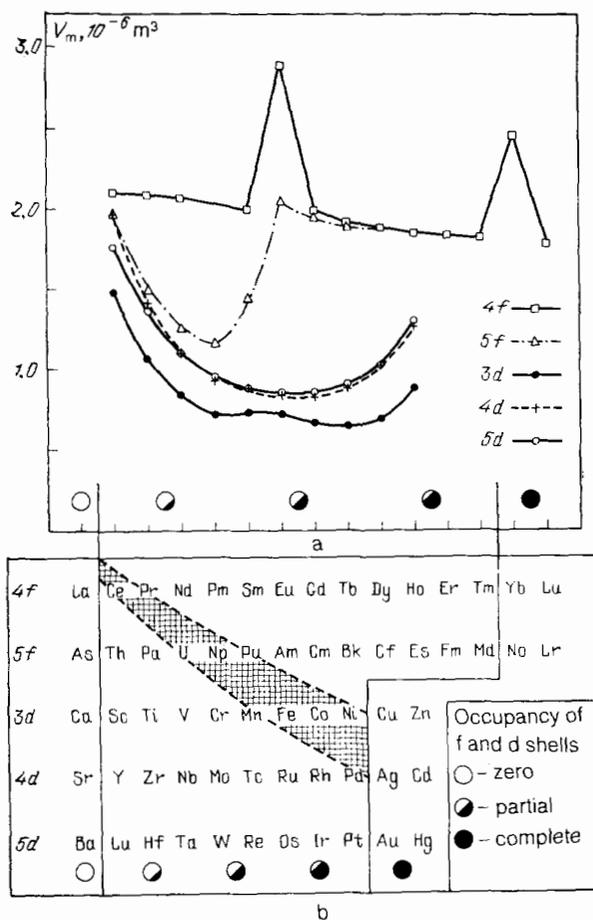


FIG. 2. Dependence of the molar volume on the atomic number for transition metals in the 4f, 5f, 3d, 4d, and 5d groups<sup>12</sup> (a) and the periodic table of transition metals<sup>13</sup> (b).

evidence of the existence of a kind of the Mott phase transition in the 5f-electron system.<sup>15</sup> There are two essentially equivalent methods of describing this situation: we can use the geometric characteristics (sizes of electron shells, etc.) or we can apply the Hubbard model based on the energy parameters of the system (band gaps, etc.). The Mott transition occurs when the screening length  $1/\lambda$  of the Coulomb potential of the ion core by the conduction electrons becomes greater than the radius of the 5f orbit  $\langle r_{5f} \rangle$  as the density of the 5f electrons is increased. As soon as the metallic radius exceeds this critical value, a cooperative modification of the structure of the 5f-electron energy band takes place and the degree of localization of the 5f electrons changes radically.

The Hubbard model utilizes the width  $W$  of a band, representing the energy of a "jump" of a 5f electron from one ion to another, and the intra-atomic Coulomb energy  $Q$  of repulsion between electrons with opposite spins but located in the same orbital. If the ratio  $Q/W$  is small, the electrons are in the collective state. If  $Q \approx W$ , then the metal-insulator transition occurs in the 5f-electron system.

Table II gives estimates of the parameter  $Q/W$  and of

$$b = \langle r_{5f} \rangle \left( \frac{4\pi}{3} R_{WS}^3 \right)^{-1/3},$$

where  $R_{WS}$  is the radius of the Wigner-Seitz sphere, indicat-

TABLE II. Parameters of electron structure of actinide metals.

Parameter	Th	Pa	U	Np	Pu	Am	Cm	Bk
$Q/W_b$	0,3 0,28	(0,4) 0,28	0,6 0,28	0,7 0,28	1,8 0,26	50 0,22	50 0,21	50 0,20

ing a major change in these parameters on transition from plutonium to americium and demonstrating that the 5f electrons are localized in americium and in heavier transuranides. This conclusion is supported by calculations of the energy structure, which show that in the case of americium, curium, berkelium, and californium the 5f levels form a narrow energy band located below the Fermi level.<sup>9,11</sup> A direct proof of the localization of the 5f electrons in americium is the observation of a line corresponding to this band in photoemission spectra.<sup>16</sup> A theoretical description of many physical properties of actinide metals based on the above ideas is in good agreement with the experimental results.<sup>17</sup>

The Mott transition in 5f-electron systems is the most characteristic effect not only of pure actinides but also of their compounds (as discussed below).

### 3. MAGNETIC PROPERTIES OF ACTINIDES

It follows from the above data that the 5f electrons in light actinides are not localized. These actinides exhibit a strong overlap of the wave functions of the 5f, 6d, and 7s electrons. Calculations reported in Ref. 11 demonstrate that in metallic thorium, uranium, neptunium, and plutonium hybridization induces a shared band of the 5f and higher-lying electrons and the width of this band is 2–3 eV (in the case of lanthanides the width of the 4f-electron band is less than 0.3 eV). Therefore, magnetic properties of these metals should be described well by the band model. It follows from the band structure calculations and from measurements of the electron specific heat and other properties that the density of states at the Fermi level  $N(E_F)$  of light actinides is relatively low (2–10 states  $\cdot eV^{-1} \cdot spin^{-1}$ ).<sup>18</sup> The Stoner criterion for the band ferromagnetism

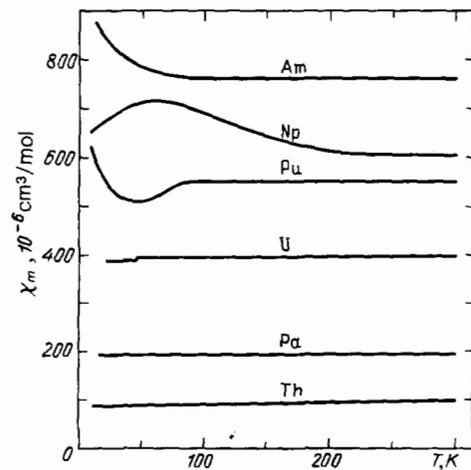


FIG. 3. Temperature dependences of the paramagnetic susceptibility of light actinides.<sup>19</sup>

$$IN(E_F) > 1 \quad (1)$$

( $I$  is the exchange interaction integral) is not satisfied by light actinides and they are exchange-enhanced Pauli paramagnetic substances.

In fact, magnetic measurements have shown that the susceptibility of light actinides is low and it depends weakly on temperature (Fig. 3).<sup>3,19</sup> The susceptibility of an exchange-enhanced band paramagnetic material is

$$\chi = \chi_0 (1 - I\chi_0)^{-1}, \quad (2)$$

where  $\chi_0 \propto N(E_F)$  is the susceptibility deduced without allowance for the exchange interaction. It follows from Fig. 3 that the susceptibility of light actinides increases on increase in the atomic number. This is due to a gradual increase in the density of states at the Fermi level. This conclusion is supported by an analysis<sup>18</sup> of the data on the electron specific heat of light actinides. An increase in the density of states  $N(E_F)$  makes neptunium and plutonium "almost magnetic" and spin fluctuations begin to play an important role in these metals. It is possible that spin fluctuations are also responsible for the low-temperature anomalies of the susceptibility of neptunium and plutonium (Fig. 3).

The most striking manifestation of the effects due to spin fluctuations are found in the transport properties of light actinides.<sup>18</sup> Figure 4 gives the temperature dependences of the electrical resistivity of actinides between thorium and plutonium. Thorium, protactinium, and uranium behave as normal metals. An increase in the resistivity on increase in the atomic number of actinides is due to an increase in the strength of magnetic scattering. The resistivities of neptunium and plutonium behave anomalously. At low temperatures these resistivities are proportional to  $T^2$  and they exhibit saturation (in the case of plutonium there is even a reduction in the resistivity) at high temperatures. This behavior can be explained using the model of spin fluctuations. Good agreement with this model has been obtained, in particular, for plutonium<sup>20</sup> if it is assumed that the Stoner exchange-enhancement factor

$$S = [1 - IN(E_F)]^{-1} \quad (3)$$

is 10 and the Fermi temperature of the 5f energy band is low (of the order of 300 K).

The magnetic susceptibility of americium, like the susceptibility of lighter actinides, depends weakly on temperature (Fig. 3).<sup>11</sup> However, the properties of americium can be interpreted in the model of localized 5f electrons if we as-

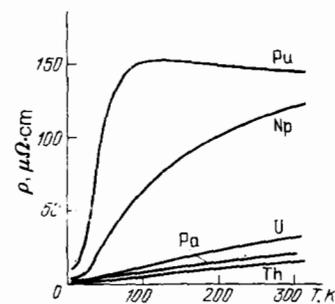


FIG. 4. Temperature dependences of the electrical resistivity of light actinides.<sup>18</sup>

sume that in the metallic state americium is trivalent and its electron configuration is  $5f^6$  with zero total angular momentum  $J$ , exactly as in the case of trivalent europium. Consequently, the magnetic moment of the ground state  $gJ\mu_B$  of americium is zero. Since the first excited state with  $J = 1$  lies at least 500 K higher than the ground state with  $J = 0$ , this metal is a typical Van Vleck paramagnetic material with a temperature-independent magnetic susceptibility.

We can therefore say that americium begins the group of actinides whose magnetic properties can be described by the model of localized  $5f$  electrons. In fact, the susceptibility of curium ( $\alpha$  modification with the double close-packed hexagonal structure), berkelium and californium (heavier actinides have hardly been investigated) obeys the Curie-Weiss law at high temperatures.<sup>21-27</sup> It follows from Table III that the effective magnetic moments of these metals are close to the effective moments of the corresponding trivalent ions (with the  $5f^7$  configuration for  $\text{Cm}^{3+}$ ,  $5f^8$  for  $\text{Bk}^{3+}$ , and  $5f^9$  for  $\text{Cf}^{3+}$ ) calculated theoretically in the Russell-Saunders approximation. Consequently, this group of actinides exhibits the Russell-Saunders coupling between the orbital and spin angular momenta, and  $J$  is a good quantum number.

The susceptibility of  $\alpha$  curium<sup>28</sup> passes through a maximum at about 50 K (Fig. 5). Neutron-diffraction investigations<sup>29</sup> have shown that this anomaly is due to the transition of  $\alpha$  curium to the antiferromagnetic state, which is described by the wave vector  $\mathbf{k} = (0, 0, 1/2)$  (characterized by doubling of the unit cell period along the hexagonal axis).

On the other hand,  $\beta$  curium with the fcc lattice (this modification is obtained by rapid cooling of the melt to room temperature) goes over to a magnetically ordered state below approximately 205 K and the net value of the saturation magnetic moment of this state differs from zero and amounts to  $0.4 \mu_B$ . In the paramagnetic range the susceptibility does not follow the Curie-Weiss law, but the Néel law:

$$\chi = \frac{(C_1 + C_2)T - 2\lambda C_1 C_2}{T^2 - T_N^2}, \quad (4)$$

where  $C_j = N\mu_{\text{eff},j}^2/6k$  are the Curie constants of two different sublattices;  $\mu_{\text{eff},j}$  are the effective magnetic moments of the sublattices (see Table III);  $\lambda = 231 \pm 49$  is the intersub-

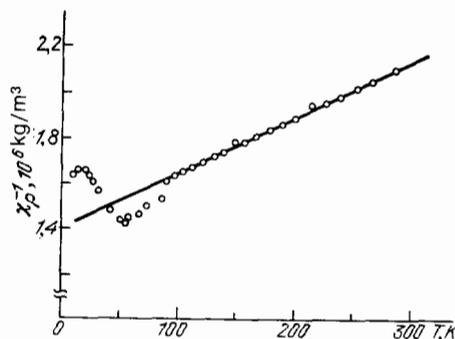


FIG. 5. Temperature dependence of the reciprocal of the susceptibility of  $\alpha$  curium.<sup>28</sup>

lattice exchange interaction constant. Using these results, it was concluded in Ref. 24 that at low temperatures the cubic modification of curium has a ferrimagnetic (or possibly non-collinear) magnetic structure.

The  $\alpha$  modification of berkelium undergoes a transition to an antiferromagnetic state.<sup>25</sup> Different values of the Néel temperature and of the paramagnetic Curie temperature of this metal are given in Refs. 21 and 30 (see Table III).

The  $\beta$  forms of berkelium and californium with the cubic structure do not exhibit magnetic ordering.<sup>22</sup>

Information on the magnetic properties of the hexagonal  $\alpha$  californium is contradictory. It was reported briefly in Ref. 26 that this modification of californium exhibits two magnetic transitions. At 59–66 K (depending on the applied field)  $\alpha$  californium goes over to an antiferromagnetic state, which below 32 K changes to the ferromagnetic or ferrimagnetic order. Both magnetic transitions are reported to exhibit a hysteresis on the temperature scale. However, the antiferromagnetic order was not observed in Ref. 27: it was reported that  $\alpha$  californium goes over to a ferromagnetic or a ferrimagnetic state below 51 K; the saturation value of the magnetic moment is  $6.1 \mu_B$ .

According to the preliminary data of Ref. 26, einsteinium shows no magnetic ordering.

In the case of some actinide metals and generally in any situation characterized by the duality of localization and

TABLE III. Magnetic properties of curium, berkelium, and californium.

Metal	Crystal modification	Effective magnetic moment $\mu_{\text{eff}}$ , units of $\mu_B$		Paramagnetic Curie temperature $\theta_p$ , K	Curie temperature $T_C$ , K	Néel temperature $T_N$ , K	Saturation atomic magnetic moment $\mu_s$ , units of $\mu_B$	Ref.
		exper.	theory					
Cm	$\alpha$	8,1	7,94	-386		52		28
	$\beta$	6,5						
Bk	$\alpha$	5,7	9,72	-183		205 *)	0,4	24
		9,67						
Cf	$\alpha$	9,7	10,63	-40	51	59-66	6,1	27
		10,7						
	$\beta$	9,8		-2--16	32			26
								22

Here, the  $\alpha$  phase has the double hexagonal close-packed structure and the  $\beta$  phase has the fcc structure.

\*) Ferrimagnetic or noncollinear ordering.

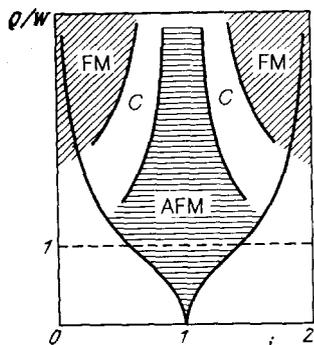


FIG. 6. Magnetic phase diagram in the Hubbard model<sup>32</sup>; FM, C, and AFM denote ferromagnetic, canted, and antiferromagnetic structures, respectively.

collectivization of the f electrons it is possible to describe a change in the magnetic properties of a metal by the Hubbard model.<sup>31</sup> Figure 6 shows the results of one of the calculations<sup>32</sup> of a magnetic phase diagram on the basis of this model. The coordinates represent the parameter  $Q/W$  (see above) and the number of electrons per atom  $i$ , which in the Hubbard model lies within the range  $0 < i < 2$ . An increase of the ratio  $Q/W$  thus corresponds to enhancement of the local-

ization. The shaded regions represent ferromagnetic and antiferromagnetic states (denoted by FM and AFM, respectively, in Fig. 6). In addition to these simple forms of magnetic ordering, the Hubbard model can deal also with more complex magnetic configurations such as a "canted" structure of the ferromagnetic helix type (denoted by C in Fig. 6). Structures of this type are frequently encountered in heavy rare-earth metals. We can expect them also in the case of heavy actinides. This diagram of magnetic phases deduced using the Hubbard model demonstrates clearly that an increase in the degree of localization of the 5f electrons increases considerably the probability of formation of various types of magnetically ordered states.

Summarizing the above, we can draw the conclusion that, because of the difficulties encountered in experimental investigations of transuranium elements (high toxicity, short half-life, strong radioactivity, etc.), the precision and reliability of the data obtained so far is still poor and significant improvements in our information on magnetic ordering in heavy actinides can be expected, but from the theoretical point of view the problem of localization and delocalization of the 5f electrons and of the nature of magnetism in various actinide metals can be regarded as settled, at least qualitatively.

TABLE IV. Valence states of actinides, lanthanides, and 3d transition metals (+ is a stable form, ⊕ is the most stable form, and ± is an unstable form).

a) 5f elements

Valence state	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
7					+	±	±								
6				⊕	+	±	±								
5			⊕	⊕	+	±	±								
4		⊕	⊕	⊕	+	±	±		+	±					
3	⊕	±	±	+	+	⊕	±	±	⊕	±	⊕	⊕	⊕	±	⊕
2						+	±				±		+		
1															

b) 4f elements

Valence state	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tu	Yb	Lu
7														
6														
5														
4		+	+					+						
3	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕
2	±		±	±	±	±						±	±	
1						±							+	

c) 3d elements

Valence state	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
7										
6										
5			⊕	⊕	⊕	⊕				
4		⊕	+	+	+	+				
3	⊕	±	+	+	+	+	⊕	±	±	⊕
2								⊕	⊕	
1										

#### 4. VALENCE OF ACTINIDES IN COMPOUNDS

The optimistic conclusion at the end of the preceding section does not apply to actinide compounds and intermetallics because studies of the electron structure of these materials are just beginning.

The similarity of various electron states in actinide atoms has a consequence that the valence of actinides in compounds can vary within a wide range from 1+ to 7+ (Ref. 33). The valence properties of actinides are closer to those of the 3d transition metals than to those of rare earths, which are characterized mainly by the valence of 3+ (Table IV).

The great variety of possible valence states of actinides makes it difficult to interpret their electron structure and magnetic properties in different compounds. The difficulties are magnified by the fact that the magnetic moments of actinides in different valence states are similar. For example, according to the Russell-Saunders approximation the effective magnetic moment of  $Cf^{2+}$  is  $10.18 \mu_B$ , that of  $Cf^{3+}$  is  $10.63 \mu_B$ , whereas  $U^{3+}$  and  $U^{4+}$  have magnetic moments of  $3.62$  and  $3.58 \mu_B$ , etc. Consequently, we cannot use magnetic measurements to determine the valence of actinides of compounds particularly since the values of the magnetic moments may be affected by the crystal fields. Moreover, the question of the validity of the  $L-S$  coupling approximation and of the Hund rule in the case of the electron states of actinides in various compounds has been questioned. The problem has been at least partly resolved<sup>26,34</sup> by showing that in the case of ionic compounds in which the valence of the actinides and, consequently, their electron state are rigidly fixed, the effective magnetic moments agree satisfactorily in most cases with the theoretical values calculated in the Russell-Saunders approximation (Fig. 7). However, in the case of these compounds the experimental values of the effective magnetic moments differ from those found by calculation. This is particularly true of the ions in the  $5f^6$  state for which the theoretical magnetic moment is zero. Investi-

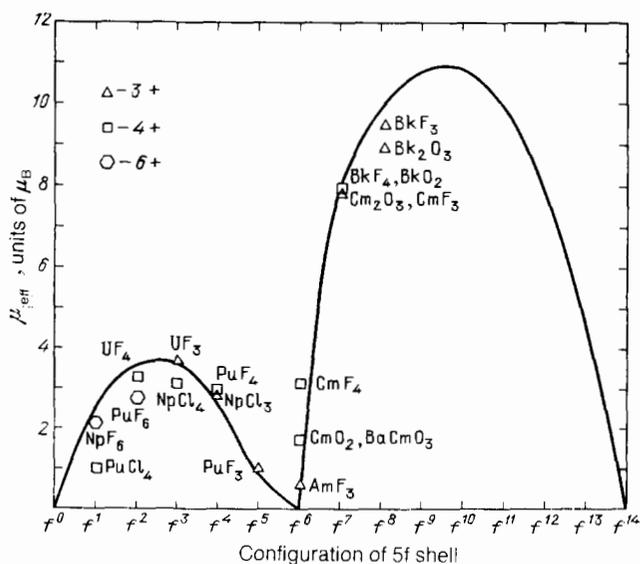


FIG. 7. Dependence of the effective magnetic moment on the configuration of the 5f shell plotted for different ionic actinide compounds.<sup>26,34</sup> The symbols represent the experimental data and the curve is plotted using the Russell-Saunders approximation.

gations of the optical absorption spectra<sup>34</sup> have shown that this discrepancy is not due to the presence of excited energy levels close to the ground state or due to the influence of crystal fields. Clearly, the  $5f^6$  state is affected significantly by the hybridization of the 5f electrons with other electron groups.

The situation is less clear in actinide compounds with covalent and metallic binding. In this case the information on the valence state of an actinide can be obtained by comparing magnetic, electrical, and other properties. Such a comparison has been made some time ago in the case of uranium monopnictides and monochalcogenides.<sup>35</sup> It was shown there that many of their properties can be explained on the assumption that uranium is in the same (trivalent or quadrivalent) valence state in all these compounds. However, the situation is more complex. This has been deduced from measurements of the magnetic form factor by the neutron scattering method. This method is the most direct technique for the determination of the valence and it makes it possible to estimate the influence of the crystal field on the state of an actinide and to determine the validity of various schemes for coupling of the orbital and spin momenta (Russell-Saunders,  $J-J$ , intermediate). In the case of uranium sulfide (US) the best agreement between the calculated and experimental values of the form factor is obtained if we assume that uranium is quadrivalent (with the  $5f^2$  configuration). However, measurements of the form factor of USb show that uranium in this compound is trivalent and has the  $5f^3$  configuration.<sup>36,37</sup>

Determination of the magnetic form factor has been used to find the valence of an actinide also in other compounds. For example, this method was used to demonstrate that the valence of uranium in  $UGa_2$  is four.<sup>38</sup>

More extensive use of this method is difficult because in the majority of cases the form factors of different electron configurations of actinides are similar and therefore determination of the state of an actinide would require a very high experimental precision. The situation simplifies only in a few cases. This is illustrated in Fig. 8 which shows the form factor of plutonium in the compound PuSb (Ref. 39). Similar

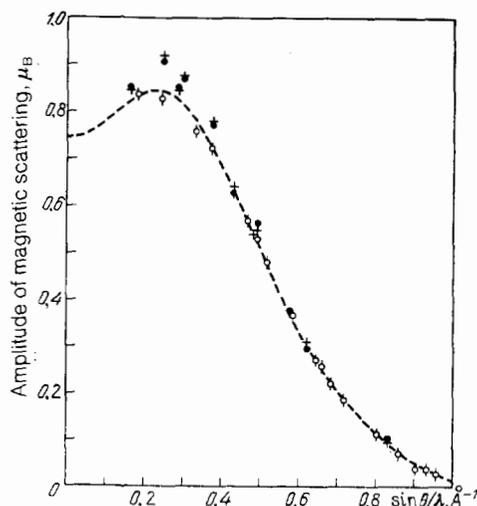


FIG. 8. Form factor of plutonium in PuSb (Ref. 39). The symbols represent the experimental data and the dashed curve is calculated for  $Pu^{3+}$  ( $5f^3$  state).

data have been obtained for the form factor of plutonium in PuP (Ref. 40). The unusual dependence of the amplitude of the magnetic scattering of neutrons of wavelength  $\lambda$  on the scattering angle  $\theta$  with a maximum at  $\sin\theta/\lambda = 0.2 \text{ \AA}^{-1}$  is a clear indication that plutonium in these compounds is in the trivalent  $5f^5$  state. In this state the total angular momentum  $J = L - S = 5/2$  is small because the large orbital angular momentum  $L = 5$  is partly compensated by the antiparallel spin angular momentum  $S = 5/2$ . The maximum in the dependence of the scattering amplitude on  $\sin\theta/\lambda$  is due to the fact that in real space the spin density is more extended than the orbital density.

The phenomenon of mixed valence in actinides has been discussed extensively.<sup>10,41</sup> The intermediate valence theory accounts, for example, for the deviation of the crystal lattice parameter from the Vegard law and for the strong rise of the coefficient of the electron specific heat of compounds  $\text{UNi}_{5-x}\text{Cu}_x$  in the range  $x > 4$  (Fig. 9),<sup>42,43</sup> and also for the behavior of the magnetic susceptibility of these compounds.<sup>44</sup> because it is postulated that an increase in the copper concentration induces a transition of uranium from the  $\text{U}^{4+} (5f^2)$  state to  $\text{U}^{3+} (5f^3)$ . The conclusion on the mixed valence of uranium in the  $\text{UNi}_{5-x}\text{Cu}_x$  system is confirmed also by the results<sup>45</sup> of an investigation of x-ray photoelectron emission spectra of these compounds. However, application of the same method combined with an analysis of the orientation of the photoelectron spin<sup>46</sup> failed to reveal effects associated with the mixed valence in the case of the compound  $\text{UNi}_{4.1}\text{Cu}_{0.9}$ . Further investigations are clearly needed.

The mixed valence model accounts also for the transition from the ferromagnetic to the antiferromagnetic ordering in NpC on increase in temperature.<sup>47</sup> This transition is due to a change in the degree of collectivization of the 5f electrons on increase in temperature, which alters the electron configuration of neptunium from  $5f^2$  at 0 K to  $5f^3$  at the temperature  $T_C$  of the magnetic phase transition.<sup>48,49</sup> The change in the valence state alters the magnetic moment of neptunium in NpC and changes the electrical resistivity of this compound at the magnetic transition point.

We can give several more examples of the mixed valence of actinide compounds. Measurements of the susceptibility have led to the conclusion that the valence of uranium in  $\text{U}_3\text{S}_5$  is mixed,<sup>50</sup> whereas a study of the crystal structure of  $\text{U}_3\text{Se}_4$  demonstrates<sup>51</sup> that uranium in this compound is in the

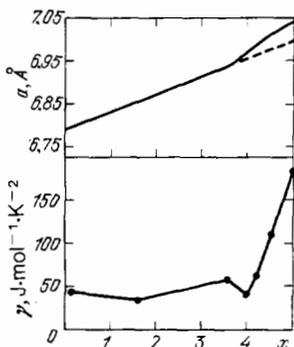


FIG. 9. Dependences of the crystal lattice parameter  $a$  and of the coefficient  $\gamma$  of the electron specific heat on the concentration of copper  $x$  in mixed intermetallic  $\text{UNi}_{5-x}\text{Cu}_x$  compounds.<sup>42,43</sup>

state  $\text{U}^{2.76+}$ . It follows from the phonon spectra<sup>52,53</sup> that uranium mononictides and monochalcogenides can also exhibit a mixed valence state ( $\text{U}^{(3-\delta)+}$ , where  $\delta = 0.3$ ). In a discussion Kasuya explained<sup>54</sup> the mixed valence of uranium in these compounds by covalent mixing of the states of the p electrons of the anion and the 5f electrons of uranium (for details see Sec. 8).

We shall now list the differences of the manifestations of the mixed valence in actinide compounds from the similar manifestations in the case of rare-earth compounds. Firstly, changes in the valence state of actinide compounds are associated with much smaller (than in the case of rare-earth compounds) changes in the crystal lattice parameters (volume anomalies) and, secondly, mixed-valence actinide compounds are frequently ferromagnetic or antiferromagnetic substances (in the case of rare-earth compounds exhibiting mixed valence the magnetic ordering is very infrequent). These differences are explained by the model of Robinson and Erdős.<sup>48,49</sup> In the final analysis, the differences are due to the different localizations of the 5f and 4f electrons.

## 5. MAGNETIC PROPERTIES OF ACTINIDE COMPOUNDS. HILL DIAGRAM

As in the case of actinide metals discussed above, the key feature governing the magnetic properties of actinide compounds is the degree of localization of the 5f electrons. This parameter in turn depends primarily on the distance  $d_{\text{An}}$  between the nearest actinide atoms in a crystal or, more exactly, it depends on the ratio of the average radius  $\langle r_{5f} \rangle$  of the 5f shell of an actinide to half the distance between the nearest actinide compounds  $R = d_{\text{An}}/2$ . The dependence of the magnetic properties of actinide compounds on the interatomic distance  $d_{\text{An}}$  was first pointed out in 1970 by Hill<sup>55</sup> who generalized and analyzed systematically the then available experimental data on the magnetic properties of uranium, neptunium, and plutonium compounds. Figure 10

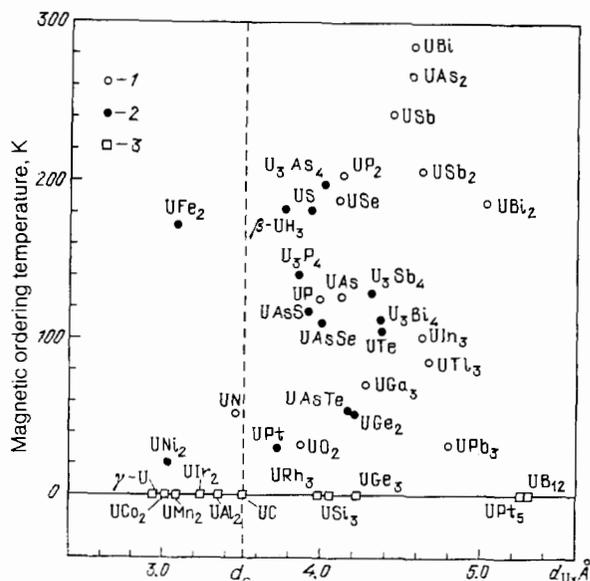


FIG. 10. Hill diagram for uranium compounds showing the dependence of the magnetic ordering temperature on the uranium-uranium distance  $d_U$ : 1) antiferromagnetic ordering; 2) ferromagnetic ordering; 3) temperature-independent paramagnetism (no ordering). The dashed vertical line represents the critical distance  $d_c$ .

TABLE V. Magnetic properties of intermetallics  $AnM_2$  ( $M = Mn, Fe, Ni, Co$ ).

Compound	$d_{An}, \text{\AA}$	Type of magnetic ordering	$T_C (T_N), \text{K}$	Saturation moment per formula unit, $\mu_B$
$UMn_2$	0,310	P	—	—
$UFe_2$	0,305	F	182	1,09
$UNi_2$	0,3045	F	21	0,12
$UCo_2$	0,303	P	—	—
$NpMn_2$	0,313	F	18	0,4
$NpFe_2$	0,309	F	492	2,8
$NpNi_2$	0,3075	F	32	1,0
$NpCo_2$	0,3045	AF	15	1,0
$PuMn_2$	0,315	F	—	—
$PuFe_2$	0,311	F	564	2,27
$PuNi_2$	0,309	P	—	—
$PuCo_2$	0,307	P	—	—

Here, P is temperature-independent paramagnetism, F is ferromagnetism, and AF is antiferromagnetism.

shows what is known as the Hill diagram for uranium compounds in which the magnetic transition temperatures are plotted as a function of the values of  $d_{An}$ . We can see that as a rule we can expect magnetic ordering in compounds for which  $d_{An}$  exceeds a certain critical value  $d_c$  (for uranium compounds this value is  $d_c \approx 3.5 \text{ \AA}$ ). In the case of compounds with  $d_{An} < d_c$  we can expect the Pauli paramagnetism, weakly dependent on temperature, and the superconductivity. A similar correlation between the magnetic properties and the distance between actinide atoms has been observed also for neptunium ( $d_c \approx 3.2 \text{ \AA}$ ) and plutonium ( $d_c \approx 3.4 \text{ \AA}$ ) compounds. It is exhibited also by compounds of one of the rare-earth metals (cerium).

The existence in the Hill diagrams of a critical distance  $d_c$  and of a sharp boundary between actinide elements with collective (itinerant) and localized 5f electrons (see above) can be explained by the Mott phase transition in the 5f-electron subsystem. This transition is related also to the tendency for the magnetic order to increase in the range  $d_{An} > d_c$ , which can be explained—as shown above—on the basis of the Hubbard model.

The Hill diagrams thus demonstrate that the behavior of the 5f electrons in compounds of light actinides is determined mainly by the degree of overlap of their wave functions, which depends mainly on geometric factors. The chemical environment of an actinide atom plays a lesser role, but its influence sometimes results in deviation from the Hill rule. An analysis of the exceptions makes it possible to refine the Hill concept.

These exceptions include intermetallic compounds of actinides with the "magnetic" 3d metals which are manganese, iron, cobalt, and nickel. By way of example, Table V gives the magnetic properties of intermetallic compounds with the formula  $AnM_2$  ( $M$  is a 3d element) and the cubic structure of the  $MgCu_2$  Laves phase type (C15).<sup>56</sup> In these compounds the distance between the nearest actinide atoms is  $d_{An} < d_c$ , but some of them are magnetically ordered and there is no simple relationship between the changes in the properties and the variation of  $d_{An}$ . This situation is due to the fact that in the case of compounds of the  $AnM_2$  type the 5f and 6d electrons of the actinide are hybridized with one

another and with the 3d electrons of the transition metal. Consequently, a hybrid energy band with a complex dependence of the density of states  $N(E)$  on the energy is formed (Fig. 11).<sup>56</sup> The Fermi level shifts toward higher values on transition from compounds of iron to compounds of nickel (i.e., on increase in the density of the 3d electrons). At the same time the density of states at the Fermi level  $N(E_F)$  varies nonmonotonically when one 3d metal is replaced with another (Fig. 11), which accounts for the nonmonotonic dependences of the magnetic properties of  $AnM_2$  compounds on  $d_{An}$ . In particular, the absence of magnetic ordering in  $UCo_2$  is attributed to the fact that in the case of this compound the density of states at the Fermi level is minimal and the Stoner criterion of the band ferromagnetism is not satisfied.<sup>56</sup>

In the range of distances  $d_{An}$  higher than the critical

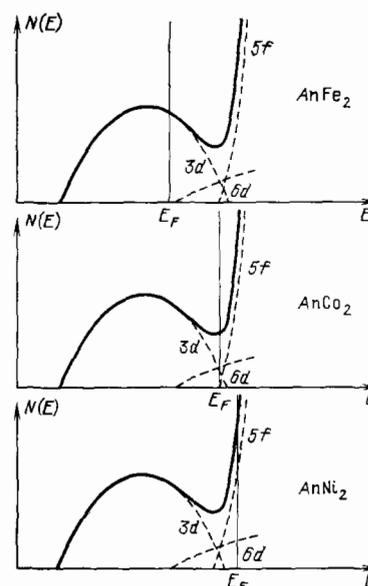


FIG. 11. Energy dependences of the density of states for compounds with the formula  $AnM_2$  ( $M = Fe, Co, Ni$ ).<sup>56</sup> Here,  $E_F$  is the Fermi level and the dashed curves represent the densities of states of different electron groups.

value there are a number of exceptions in the Hill diagrams and these behave in the manner opposite to that just described, i.e., some of these compounds are nonmagnetic although the distance between the actinide atoms in them is sufficiently large for the delocalization due to the direct overlap of the 5f orbitals. We have in mind here intermetallic compounds such as  $\text{NpRh}_3$ ,  $\text{URh}_3$ ,  $\text{UIr}_3$ ,  $\text{UGe}_3$ ,  $\text{UPt}_5$ , etc.<sup>57-60</sup> Theoretical and experimental investigations of the energy band structure of some of these compounds<sup>61-63</sup> also indicate that the delocalization of the 5f electrons, preventing the appearance of a magnetic order in these compounds, is due to hybridization with other electron groups (with the 2p electrons of germanium in  $\text{UGe}_3$ , with the 5d electrons of iridium and platinum in  $\text{UIr}_3$  and  $\text{UPt}_5$ , with the 4d electrons of rhodium in  $\text{URh}_3$ , etc.).

Another characteristic example of the situation when hybridization determines the electronic and magnetic properties of actinide materials is the intermetallic compound  $\text{UCo}_{5.3}$  ( $d_{\text{An}} \approx 4.05 \text{ \AA}$ ) whose magnetic moment in the ferromagnetic state can be explained readily on the assumption that uranium is nonmagnetic and gives up its 5f electrons to the 3d energy band of cobalt.<sup>64</sup>

Actinide compounds containing "heavy fermions" ( $\text{UBe}_{13}$ , are  $\text{UPt}_3$ , etc.) also belong to this group and are apparently the subject of major interest.<sup>65</sup> Hybridization of the 5f electrons in these compounds is responsible for the very high density of states at the Fermi level, which gives rise to anomalously large values of the coefficient of the electron specific heat ( $\gamma \sim 10^2 - 10^3 \text{ mJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-2}$ ) and, consequently, to enormous values of the effective mass  $m^*/m_e \sim 10^2 - 10^3$  ( $m_e$  is the electron mass).

The value of  $d_c$  thus divides the paramagnetic and magnetically ordered substances only in the case of absence of the hybridization of the 5f electrons with other electron groups. All the actinide compounds can be arranged on the same Hill diagram using a parameter representing the state of the 5f electrons more accurately than the interatomic distance  $d_{\text{An}}$ . In the case of actinide compounds and elements these may be the parameters  $Q/W$  and  $b$ , discussed above (see Table II). However, for the majority of actinide compounds these parameters have not yet been identified.

## 6. COMPOUNDS WITH BAND MAGNETISM

As the overlap of the wave functions of the 5f electrons in metallic actinide compounds decreases, a change takes place from the Pauli paramagnetism and superconductivity to the magnetism of localized electrons. In the region of this change (in the Hill diagram this corresponds to  $d_{\text{AN}} \approx d_c$ ) we can expect spin-fluctuation states and a weak band ferromagnetism (or antiferromagnetism) which deserves separate consideration because effects of this kind represent the special case of the phenomenon of band magnetism which is not yet fully understood.

In spite of the fact that, as mentioned in Sec. 3, delocalization of unpaired electrons (which are the 5f electrons in the case of actinides) on the whole hinders magnetic ordering, such ordering is still possible for certain parameters of the system. However, in contrast to substances with localized magnetic moments, magnetic ordering in a system of collective (itinerant) electrons has a clear "threshold": when the exchange interaction between localized electrons

decreases, magnetic order still appears at sufficiently low temperatures, whereas in a system of collective-state electrons magnetic order is induced only if the exchange interaction is sufficiently strong to satisfy the Stoner criterion [see Eq. (1)].

We can formulate a number of criteria which make it possible to assign a particular magnetically ordered substance to a class of band magnetic materials<sup>12</sup>:

a small (compared with that calculated in the approximation of localized moments and also compared with the effective moment in the paramagnetic state) magnetic moment in the magnetically ordered state;

suppression of ferromagnetism by a moderate hydrostatic pressure  $p$ , i.e., a reduction in the saturation moment  $\mu_s$  and of the magnetic ordering temperature  $T_C$  on increase in pressure:

$$\frac{d \ln \mu_s}{dp} < 0, \quad \frac{d \ln T_C}{dp} < 0, \quad (5)$$

and, moreover,<sup>66</sup>

$$\frac{d \ln \mu_s}{d \ln T_C} \approx 1; \quad (6)$$

a large value of the coefficient  $\gamma$  of the electron specific heat;

a smaller—than theoretically calculated in the model of localized moments and equal in this case to  $R \ln(2S + 1)$ —magnetic entropy;

a deviation from the Curie-Weiss law in the case of the susceptibility in the paramagnetic state;

a strong influence of substitution on the magnetic properties of a substance.

Each of these criteria separately cannot be regarded as the proof of the band nature of the magnetic ordering. Only the occurrence of most of them, together with additional information obtained from investigations of transport properties, neutron diffraction studies, spectroscopic investigations, etc., makes it possible to classify the nature of magnetic ordering.

An example of a band actinide ferromagnetic material is the intermetallic compound  $\text{UFe}_2$  mentioned above. It follows from Table VI, which lists the main magnetic properties of this compound taken from Refs. 56 and 67-69, that this material exhibits many characteristic criteria of the band magnetism (a small saturation moment, a large ratio of the effective moment to the saturation moment, a considerable temperature-independent contribution to the paramagnetic susceptibility, a large value of the coefficient of the electron specific heat, a strong reduction in the saturation magnetization and in the Curie temperature as a result of hydrostatic compression, etc.). In the case of mixed  $\text{U}(\text{Fe}_{1-x}\text{Co}_x)_2$  compounds (where  $\text{UCo}_2$  is an exchange-enhanced band paramagnetic substance; see above) the Curie temperature decreases rapidly on increase in  $x$  and the ferromagnetism disappears in the range  $x > 0.38$  (Ref. 70). This system satisfies the Stoner-Wohlfarth relationships<sup>67,71</sup> between the saturation magnetic moment and the Curie temperature of various compositions

$$\mu_s(x) = AT_C(x), \quad (7)$$

and the relationship between the pressure dependence of the saturation moment and the saturation moment itself:

TABLE VI. Magnetic properties of intermetallic compound UFe<sub>2</sub>.

Curie temperature $T_C$ , K	Saturation atomic magnetic moment $\mu_s$ , units of $\mu_B$	Paramagnetic temperature $\theta_p$ , K	Effective magnetic moment $\mu_{eff}$ , units of $\mu_B$	Temperature-independent paramagnetic susceptibility $\chi$ , $10^{-6}$ cm <sup>3</sup> /mol	Coefficient of electron specific heat $\gamma$ , mJ·mol <sup>-1</sup> ·K <sup>-2</sup>	$\frac{d \ln T_C}{dp}$ , Mbar <sup>-1</sup>	$\frac{d \ln \mu_s}{dp}$ , Mbar <sup>-1</sup>
162	1,09	169	3,03	988—1200	55	-3	-5

$$\frac{d \ln \mu_s(x)}{dp} = B \mu_s^{-2}(x). \quad (8)$$

These relationships follow from a phenomenological theory of a weak band ferromagnetism.<sup>72</sup>

The most detailed investigations of the band ferromagnetism have been carried out<sup>67,73-75</sup> on the intermetallic compound UPt (with the orthorhombic crystal structure of the CrB type). Near its equiatomic composition there is a narrow range of homogeneity where, depending on the stoichiometry, the saturation moment ranges from 0.05 to 0.5  $\mu_B$ , i.e., it varies by a factor of 10, whereas the effective moment of all the compounds is approximately 3.5  $\mu_B$ . The compound UPt has a large coefficient of the electron specific heat amounting to 110 mJ·mol<sup>-1</sup>·K<sup>-2</sup>. Important information has been obtained from photoelectron spectra of various intermetallic compounds belonging to the uranium-platinum system.<sup>76</sup> These spectra are typical of intermetallic compounds of actinides with transition metals. In the case of these compounds there is a strong (compared with metallic platinum) reduction in the width of the 5d energy band and some reduction in the intensity of the corresponding lines in the photoelectron spectrum. These effects are clearly associated with a reduction in the overlap of the outer orbitals and with the 5f and 6d hybridization in the formation of these compounds, although these experiments have failed to reveal a direct contribution to photoemission from the 6d electrons when only one x-ray line ( $K_\alpha$  of Al) was used. The line corresponding to the 5f electrons has practically the same position and intensity for metallic uranium and for the compound UPt. Since in metallic uranium the 5f electrons are in the collective state, this confirms the band nature of the 5f electrons in the compound UPt.

However, there are experimental data indicating that the properties of UPt cannot be described by a simple model

of a weak band ferromagnetic material. This compound clearly has a complex magnetic structure<sup>12</sup>; the magnetic contribution to the entropy, although five times less than that calculated in the model of localized moments, is still larger than in the case of other weak band ferromagnetic substances. The relationship (6) for ferromagnetic substances with collective-state (itinerant) carriers<sup>66</sup> and other criteria are not satisfied by UPt.

We can give also other examples of the use of the model of band ferromagnetism in the description of the properties of actinides. For example, the regular variation of the magnetic properties of the NpRu<sub>2</sub>-NpOs<sub>2</sub> quasibinary system from paramagnetism of NpRu<sub>2</sub> to ferromagnetism of NpOs<sub>2</sub> can be described satisfactorily by this model.<sup>77</sup>

We have already mentioned that in the case of metallic neptunium and plutonium, which are magnetically disordered but in which the density of states at the Fermi level is sufficiently high, there are some important effects due to spin fluctuations. Such spin-fluctuation effects have been observed also in a number of magnetically almost ordered actinide compounds (UA<sub>12</sub>, UA<sub>13</sub>, UCo<sub>2</sub>, UPt<sub>3</sub>).<sup>78</sup> The low-temperature electrical resistivity of these compounds, like that of neptunium and plutonium, is proportional to  $T^2$ , there is a logarithmic contribution to the specific heat, etc. Reduction in the slope of the magnetization curves in strong fields, due to the appearance of spin fluctuations in such fields, is very typical of band ferromagnetics with spin fluctuations. In the case of UA<sub>12</sub> this effect is observed at low temperatures in fields 100–150 kOe (Fig. 12).<sup>79</sup> The differential susceptibility observed in strong fields becomes equal to the initial susceptibility of UA<sub>12</sub> at temperatures above the characteristic temperature for the appearance of spin fluctuations  $T_{sf} \approx 20$  K, above which these fluctuations are thermally suppressed.

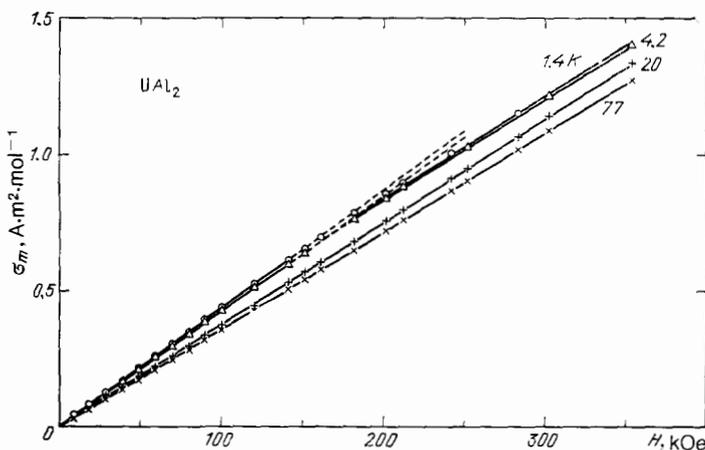


FIG. 12. Field dependences of the magnetization of UA<sub>12</sub> at different temperatures.<sup>79</sup>

We shall conclude this section by noting that band magnetism of actinide compounds has not yet been investigated sufficiently thoroughly. In most cases an analysis of the available experimental data has been made qualitatively and there are practically no quantitative models for the description of actinide band magnetic materials.

This is mainly due to the complexity of the electron structure and it applies also to actinide magnetic materials with almost-localized 5f electrons.

## 7. MAGNETIC PROPERTIES OF COMPOUNDS WITH ALMOST-LOCALIZED 5f ELECTRONS

During the early stages of the study of actinide compounds concerned mainly with magnetic properties the localization of the 5f electrons has been deduced, firstly, from the Hill diagram (i.e., from the actinide-actinide distance in the crystal lattice) and, secondly, by comparing the properties of actinides with the properties of rare-earth magnetic materials in which, as is well known, the 4f electrons are almost always localized. Therefore, the values of the magnetic moment in a magnetically ordered state close to those calculated theoretically for a free ion, the Curie-Weiss law obeyed in the paramagnetic phase, the approximate equality of the effective magnetic moment in a paramagnetic phase and of the magnetic moment in a magnetically ordered state, giant values of the magnetic anisotropy and magnetostriction, etc., have been the "external" criteria demonstrating the localization of the 5f electrons in actinide compounds. Two alternative models of total localization or total delocalization of the 5f electrons have been used.

Subsequently, when the electron structure of actinide compounds has been investigated not only by determination of magnetic properties, but also by such fine investigation methods as optical spectroscopy in a wide range of wavelengths, photoemission and x-ray spectroscopic measurements using synchrotron radiation, neutron elastic and inelastic scattering, etc., it became clear that the situation is more complex. It has been found that the total localization of the 5f electrons is hardly ever (at least in the case of compounds of light actinides) found in reality even in those compounds which on the basis of magnetic measurements should be characterized by the total localization of the 5f electrons and an overlap of the 5f-electron functions with the wave functions of other groups of electrons.

The fullest (but still incomplete) information is available on the magnetic properties and electron structure of two groups of monocompounds of light actinides: mononpnictides  $AnX$  ( $X = N, P, As, Sb$ ) and monochalcogenides  $AnY$  ( $Y = S, Se, Te$ ). These groups have been tackled first because actinide mononpnictides and monochalcogenides have a simple crystal structure (bcc lattices of the rocksalt type), many of them are available in the form of large high-quality single crystals, etc. Therefore, in discussing the properties of actinide magnetic materials with almost-localized 5f electrons we shall concentrate mainly on these two groups of compounds.

Table VII summarizes the main magnetic properties (magnetic ordering temperatures, nature of magnetic structures, values of magnetic moments) of actinide mononpnictides and monochalcogenides based on the reviews in Refs. 4, 19, and 80. We can see that the properties of these monocompounds cover a very wide range and that they depend

strongly both on the actinide and on the anion. All uranium pnictides are antiferromagnetic, whereas curium pnictides (like uranium chalcogenides) are ferromagnetic. In the case of other monocompounds there is no such clear division. For example, all the investigated neptunium monocompounds, both pnictides and chalcogenides (except for the ferromagnetic nitride  $NpN$ ) are antiferromagnetic. Among plutonium and americium monocompounds there are ferromagnetic and antiferromagnetic compounds as well as those which remain paramagnetic independently of temperature right down to low temperatures. The absence of magnetic ordering in plutonium monochalcogenides can clearly be explained by the fact that plutonium is either in the divalent state with  $J = 0$  or it is quadrivalent and has a singlet ground state in the crystal field. The paramagnetism of the compounds  $AmN$  and  $AmSb$  can be described on the assumption that the americium in them is trivalent ( $J = 0$ ). However, if this explanation is adopted, the reason for the antiferromagnetic ordering of  $AmAs$  is not clear. It may be that the magnetic moment of this compound is due to mixing (in the exchange field) of excited states and the ground nonmagnetic state, in the same way as found in, for example, compounds of trivalent europium.

The antiferromagnetic structures observed in monocompounds of light actinides vary. Most of them exhibit a commensurate magnetic ordering of the I or IA type, whereas some compounds exhibit incommensurate antiferromagnetic structures of the spin-wave type. In many cases there is a change in the nature of magnetic ordering as a result of variation of temperature. The magnetic structures of actinide monocompounds will be discussed later.

The large distances between the actinide atoms in monocompounds (3.5–4.4 Å) allow us to ignore the direct exchange mechanism in explaining the nature of magnetic ordering in these compounds. The considerable electrical conductivity of these substances, which are semimetals, makes it possible to assume that a considerable role is played in them by the indirect exchange interaction via conduction electrons, known as the Ruderman-Kittel-Kasuya-Yosida (RKKY) mechanism. In fact, the use of this mechanism in a simple model of a spherical Fermi surface for conduction electrons can account for the observation that all uranium mononpnictides are antiferromagnetic and monochalcogenides are ferromagnetic. It is assumed that uranium in these compounds is quadrivalent, i.e., that it is in the  $5f^2$  state so that in pnictides there is one conduction electron per uranium ion, whereas in chalcogenides there are two conduction electrons.<sup>35</sup>

The magnetic moment of the U atom,  $\mu_m$ , found from the magnetic data for ferromagnetic uranium monochalcogenides differs from the magnetic moment  $\mu_n$  deduced from neutron diffraction studies (Table VII). This interesting effect is explained in the RKKY model by the polarization of conduction electrons which makes a contribution  $\Delta\mu$  to the magnetic moment. Because of the delocalization of conduction electrons, this contribution does not give rise to an additional magnetic coherent scattering of neutrons, i.e., neutron diffraction measurements give only the localized part of the magnetic moment. In the case of uranium monochalcogenides the polarization of delocalized conduction electrons is antiparallel to the localized moment, and we have  $\mu_n > \mu_m$  ( $\Delta\mu < 0$ ).

TABLE VII. Magnetic properties of actinide mononictides and mono chalcogenides.<sup>\*)</sup>

Anion	Actinide														
	U			Np			Pu			Am	Cm		Bk		
N	a) Pnictides														
	AFI	53	0,75	F	82-100	1,4	ΔΦ	13	<0,3	P	F	109	—	F	88
—	—	2,66	—	—	2,13	—	—	1,5	—		—	7,02	—	—	—
P	a) AFI	b) 122	c) 1,9	SW1	130	1,8	F	126	0,77	?	F	73	—	?	?
	a) AFI	b) 23	d) —	SW2	74	2,8	—	—	0,49		—	—	—		
As	AFI	124	2,2	AFI	172,5	2,5	F	123	0,75	ΔΦ	13	—	F	88	—
	AFIA	62	—	AF?	155	—	—	—	0,67		—	—	1,14	—	—
Sb	AFI	213	2,85	AF	207	2,5	SW	85	0,74	P	F	162	—	?	?
	—	—	—	—	—	≈ 2,3	F	67	1,0		—	—	—		
Bi	AF?	285	3,0	?	?	?	AF?	65	—	?	?	?	?	?	?
	—	—	4,1				—	—	0,61						
S	b) Chalcogenides														
	F	178	1,7	AF	23	0,9	P	?	?	?	?	?			
—	—	1,55	—	—	1,49										
Se	F	160	2,0	?	?	?	P	?	?	?	?	?			
	—	—	1,81										—	—	2,4
Te	F	104	2,2	?	?	?	P	?	?	?	?	?			
	—	—	1,91										—	—	2,7

<sup>\*)</sup> The magnetic characteristics given in the columns and rows of this table are explained in the case of the actinide U and the anion P, taken as an example: a) type of magnetic ordering; b) temperatures of magnetic ordering (K); c) magnetic moment deduced from neutron diffraction (units of  $\mu_B$ ); d) magnetic moment deduced from magnetic data (units of  $\mu_B$ ); e) effective magnetic moment (units of  $\mu_B$ ). Magnetic ordering notation: F is ferromagnetic, AF is antiferromagnetic (of types I or IA), SW is antiferromagnetic ordering of the spin-wave type, P is temperature-independent paramagnetism, ? means no studies have been made, and a dash (-) means that it either does not exist or has not been investigated.

The polarization contribution to the magnetic moment of uranium monocompounds is very large (much larger than in the case of rare-earth magnetic materials) and it cannot be explained on the assumption that the 5f electrons of the actinide are fully localized. There are certain other special features of the magnetic properties of actinide pnictides and chalcogenides which cannot be described by the simple model of the RKKY interaction of the localized 5f electrons via conduction electrons. We shall consider these features in greater detail by considering uranium monocompounds which have been studied thoroughly.

Neutron diffraction studies have shown that in a magnetically ordered state the magnetic structures of uranium monopnictides are complex noncollinear configurations<sup>80,81</sup> known as multi-k structures (Fig. 13), which can be described by modifying the formula for the Fourier representation of a magnetic structure

$$\mathbf{m}_n = \sum_{\mathbf{L}} \exp(2\pi i \mathbf{k}_L \cdot \mathbf{t}_n a^{-1}) \mathbf{m}_0, \quad (9)$$

which relates the moment  $\mathbf{m}_n$  of the  $n$ th primitive cell to the moment  $\mathbf{m}_0$  of the cell chosen as the zeroth one ( $\mathbf{t}_n$  is the vector of translation between these cells and  $a$  is the crystal structure parameter) by introducing two or three wave vectors  $\mathbf{k}$  (2k and 3k structures). In zero magnetic fields the structures of uranium monopnictides have either the wave vector  $|\mathbf{k}| = 1$  (antiferromagnetic type I structure) or  $|\mathbf{k}| = 1/2$  (type IA structure). The possible antiferromagnetic structures include a collinear 1k structure (shown on the left in Fig. 13) and noncollinear 2k (Fig. 13, center) and 3k (Fig. 13, on the right) structures.

The 1k structure consists of ferromagnetically ordered (001) planes alternating in a specific sequence (+ - + - for the antiferromagnetic type I ordering and + + - - for the antiferromagnetic type IA ordering) and the moments are oriented at right-angles to these planes. The symmetry of the 1k structure is tetragonal.

In the 2k structure the magnetic moments are directed along different axes of the [110] type lying in (001) planes. This structure also has tetragonal symmetry.

The magnetic moments in the 3k structure are oriented along different directions of the [111] type and the symmetry of this structure is cubic.

It is difficult to reveal multi-k structures because the scattering of neutrons by these structures has the same effect as the scattering of neutrons by polydomain samples with

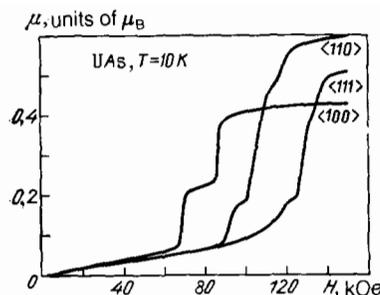


FIG. 14. Field dependences of the magnetic moment of UAs along different directions, determined at 10 K (Ref. 82).

the 1k structure. However, the application of uniaxial mechanical stresses or of a magnetic field, which makes different domains inequivalent, produces different neutron scattering patterns for different multi-k structures, so that it is possible to determine reliably the type of the structure of uranium monopnictides already under uniaxial pressures of the order of 1 kbar or in fields of about 50 kOe.

It has now been established<sup>80,81</sup> that all uranium monopnictides assume the type I ordering below the Néel temperature, but in the case of USb the structure is noncollinear of the 3k type, whereas the other pnictides have the collinear 1k structure. Cooling induces a first-order transition in UP to a phase with the noncollinear 2k structure. A similar transition is exhibited by UAs. However, in this compound it is accompanied by a change in the type of the antiferromagnetic structure from I to IA.

The antiferromagnetic structures of uranium monopnictides are of the layer type and we can expect these compounds to be metamagnetic, like other layer antiferromagnetic materials. In fact, magnetic and neutron-diffraction investigations have confirmed this hypothesis. Figure 14 shows, by way of example, the magnetization curves of a single crystal of UAs determined along different crystallographic directions.<sup>82</sup> We can see that when a field is applied this compound exhibits metamagnetic jumps of the magnetization. It is interesting to note that in fields exceeding those which induce metamagnetic transitions the magnetic moment is less than that calculated on the basis of the ferromagnetic ordering model. It is therefore suggested in Ref. 82 that in this range of fields the structure of UAs is ferrimagnetic.

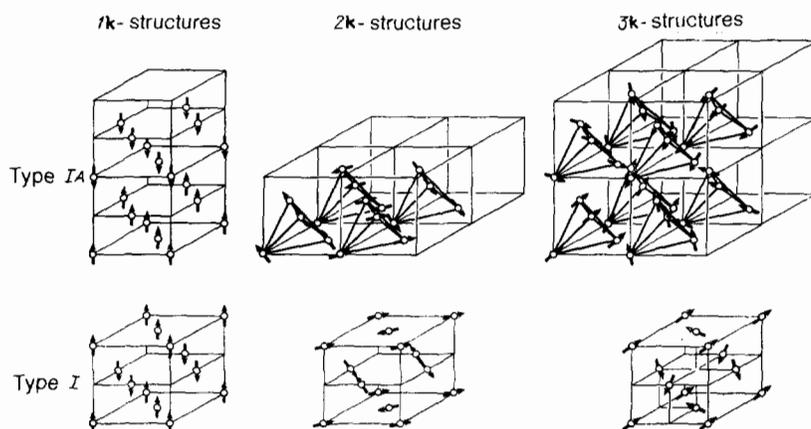


FIG. 13. Multi-k structures.<sup>80,81</sup>

The hypothesis is supported by the results of neutron-diffraction investigations of the magnetic structure of UAs in strong magnetic fields<sup>54,80</sup> and the results of these are used to plot the magnetic  $H$ - $T$  phase diagram of a single crystal of UAs in a field parallel to the [001] axis, shown in Fig. 15. At high temperatures a high-field ferrimagnetic phase denoted by 4 has the collinear 1k structure, whereas at low temperatures the application of a field induces a transition to a non-collinear 2k ferrimagnetic phase 3.

A detailed analysis of the magnetization processes along different crystallographic directions of a UAs single crystal reported in Refs. 54 and 80 shows that these and other uranium monpnictides are strongly anisotropic anti-ferromagnetic substances. The exchange between the magnetic moments located in planes of the (001) type is ferromagnetic and the much weaker interplanar exchange interactions can be ferromagnetic or antiferromagnetic. Such a planar quasitwo-dimensional magnetic structure can be described within the framework of the so-called anisotropic Ising model allowing for the interactions in several coordination spheres, suggested earlier to account for the magnetic properties of cerium monpnictides.<sup>80,81</sup> This model is based on the following one-dimensional Ising Hamiltonian:

$$\mathcal{H} = \mathcal{H}_0 - \sum_{j=1}^N \sum_{r=-\infty}^{+\infty} I(r) m_j m_{j+r} - H \sum_{j=1}^N m_j. \quad (10)$$

Here,  $\mathcal{H}_0$  is the Hamiltonian of an isolated (001) plane;  $I(r)$  is the effective interplanar exchange integral;  $N$  is the number of layers;  $|m_j| = 1$ ;  $H$  is a magnetic field directed along the [001] axis. When only the interaction between the nearest ( $I_1$ ) and the second-nearest ( $I_2$ ) planes is taken into account, the theory predicts that at 0 K the structure should be ferromagnetic if  $I_1 > 0$  and antiferromagnetic if  $I_1 < 0$ , and if  $|I_2/I_1| < 1/2$ , this is a structure of type I, whereas if  $|I_2/I_1| > 1/2$ , the structure is of type IA. Calculations carried out in the molecular field approximation demonstrate that an increase in temperature converts a type IA structure into a type I structure; this conversion is a first-order phase transition. Near the Néel temperature when certain conditions are satisfied ( $|I_2/I_1| > 1/4$ ) we can expect modulated long-period antiferromagnetic structures of the longitudinal spin-wave type (such structures are observed in compounds NpAs and PuP). The theory predicts also ferromagnetic 1k

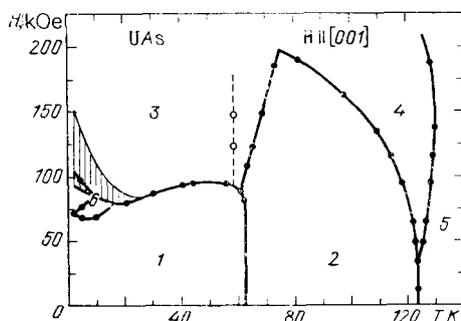


FIG. 15. Phase ( $H$ - $T$ ) diagram of UAs in a field parallel to the [001] axis.<sup>54,80</sup> Phases: 1) antiferromagnetic, 2k structure of the IA type; 2) antiferromagnetic, 1k structure of the I type; 3) ferrimagnetic, 2k structure; 4) ferrimagnetic, 1k structure; 5) paramagnetic; 6) incommensurate phases.

structures in actinide pnictides subjected to a magnetic field. However, the anisotropic Ising model discussed above cannot account for the multi- $k$  structures observed in uranium pnictides.

We shall consider briefly the magnetic properties of uranium monochalcogenides. These compounds are ferromagnetic with easy magnetization axes of the [111] type.<sup>83</sup> Their anisotropy is very strong. Measurements of the magnetization of uranium monochalcogenide single crystals in fields up to 200 kOe have demonstrated<sup>84</sup> that even in such strong fields the magnetization does not deviate from the [111] easy magnetization axis and that these compounds are Ising ferromagnetic materials.

The nature of the interactions responsible for the very strong magnetic anisotropy of actinide monpnictides and monochalcogenides is not yet understood. There have been unsuccessful attempts to account for the magnetic behavior of these compounds allowing not only for the isotropic exchange of the RKKY type, but also for the single-ion anisotropy due to the interaction of an anisotropic cloud of the localized 5f electrons with the crystal field of the lattice. Firstly, the RKKY model cannot account for such a large difference between the intraplanar and interplanar interactions which occur in monpnictides of uranium and other actinides. Secondly, the magnetic anisotropy of uranium monocompounds is approximately an order of magnitude higher than that of monocompounds of light rare earths (neodymium and praseodymium) in which it is described well by the single-ion model and, consequently, the single-ion mechanism cannot account for the anisotropy of uranium monocompounds.<sup>85</sup> Thirdly, simple considerations demonstrate<sup>86</sup> that the interaction with the crystal field in uranium monocompounds should orient the magnetic moments along axes of the [111] type and thus allowance for only this anisotropic mechanism fails to account for the 1k structures with the moments oriented along the [001] axis observed for uranium monpnictides.

All these observations and the multiaxial 2k and 3k antiferromagnetic structures of monpnictides can be explained qualitatively assuming that a second anisotropy mechanism, which is the anisotropic exchange interaction, plays an important role in uranium monocompounds, in addition to the single-ion mechanism. The competition between these two mechanisms gives rise to complex magnetic structures and to transitions between them.

At present the anisotropic exchange interaction is attributed to characteristic features of the electron structure of actinide monocompounds. We shall now describe this electron structure.

The recent optical, magneto-optic, and photoemission investigations<sup>87-89</sup> have made it possible to represent schematically the electron structure of uranium monpnictides and monochalcogenides as shown in Fig. 16 (Ref. 85). A characteristic feature of the electron structure of these compounds is a high density of the 5f states at the Fermi level, amounting to 5-6 states  $\cdot eV^{-1} \cdot spin^{-1}$ . These states form a narrow (of width of the order of 1 eV) approximately half-filled energy band which is hybridized with the wider 6d band characterized by a lower density of states. The new hybrid conduction band contains two or three 5f electrons and about one 6d electron.

This electron structure of actinide monocompounds

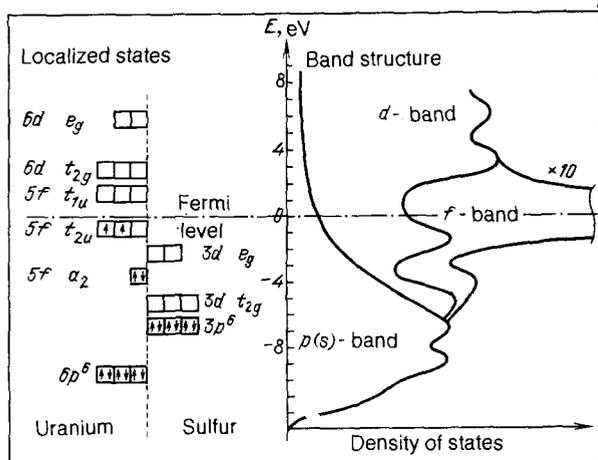


FIG. 16. Energy band structure of uranium monpnictides and monochalcogenides shown schematically for the specific case of US (Ref. 85). The corresponding localized states are shown on the left.

with partly delocalized 5f states appears because the energy of the Coulomb repulsion  $Q$  of two electrons in the 5f shell is comparable with the energy of the one-electron interaction due to the crystal field (the corresponding localized states of electrons of uranium and of the pnictogen/chalcogen are shown on the left of Fig. 16). In terms of the Hubbard model, this situation is equivalent to the case when  $Q/W \approx 1$  (see above, Fig. 6).<sup>85,90</sup>

The electron structure shown in Fig. 16 is in principle the same for all uranium monpnictides and monochalcogenides, but the degree of hybridization and the width of the 5f band depend on the distance  $d_U$  between uranium atoms in the crystal lattice. If  $d_U$  is small, the f-d hybridization effects are strong and we can regard the 5f electrons as being almost in the collective state (almost itinerant), as confirmed recently<sup>91</sup> by an investigation of photoemission of electrons from UN. An increase in  $d_U$  reduces the degree of overlap of the 5f and 6d orbitals, the hybridization effects become weaker, and (according to Ref. 92) the 5f electrons in UTe, where the distance  $d_U$  is large, can be regarded as quasilocalized.

This electron structure of uranium monocompounds explains the experimentally observed difference between the magnetic moments deduced from neutron diffraction and magnetic measurements (discussed earlier in the present section), if we assume that in these compounds the exchange interaction between quasilocalized 5f states occurs via delocalized states of the 6d type. The polarization of these delocalized states makes a negative contribution to the magnetic moment which is revealed when we compare the results of neutron-diffraction and magnetic investigations. An increase in the degree of localization of the 5f states on increase in  $d_U$  in uranium monocompounds increases the magnetic moment in magnetically ordered states and increases the ratio of this moment to the effective moment in a paramagnetic state (Fig. 17).

This picture of the f-d hybridization is the basis of a model proposed by Cooper and his colleagues<sup>93-96</sup> to explain the nature of the anisotropic exchange in monocompounds of light actinides. This model was first suggested by Coqblin and Schrieffer<sup>97</sup> for the magnetic properties of cerium mon-

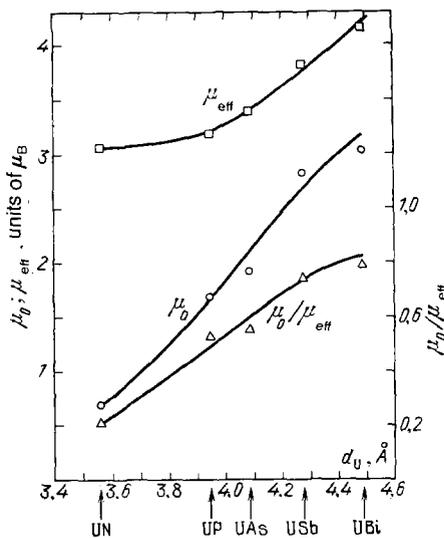


FIG. 17. Dependences of the atomic magnetic moment  $\mu_0$  in a magnetically ordered state, of the effective moment  $\mu_{\text{eff}}$ , and of the ratio  $\mu_{\text{eff}}/\mu_0$  on the uranium-uranium distance  $d_U$  for uranium monpnictides.

pnictides and is known by their name. It allows for the fact that the 6d conduction electrons have an orbital moment and it deals with the combined spin and orbit scattering of these electrons by the localized 5f states. The pair interaction between two 5f ions which appears as a result of such scattering is strongly anisotropic: it orients the magnetic moments at right-angles to the axis linking the ions. The results obtained were generalized to the crystal structure of this rocksalt type and it was found that the Coqblin-Schrieffer interaction gives rise to a considerably stronger exchange coupling between the moments of atoms in one plane of the (001) type than between the moments of atoms in different planes of this type. Moreover, it follows from this model that in the ferromagnetic ordering case the easy magnetization axes should be [111], whereas in uranium monochalcogenides in the case of the antiferromagnetic ordering the Coqblin-Schrieffer interaction orients the magnetic moments at right-angles to (001) planes, as observed in monpnictides.

The Cooper model, first developed in the one-electron approximation, has been extended subsequently to many-electron 5f atoms.<sup>95</sup> A clear success of this theory is that it accounts (allowing for the isotropic RKKY interaction and the single-ion anisotropy) for some of the multi-k structures observed in monochalcogenides. Cooper and his colleagues used this model to account also semiquantitatively for the evolution of the magnetic properties of uranium pnictides<sup>98</sup> and of PuSb crystals<sup>96</sup> observed when temperature is varied. In particular, they explained transitions between different multi-k structures in uranium pnictides UP and UAs and the transition from the ferromagnetic to the incommensurate antiferromagnetic phase in PuSb.

A different approach to the anisotropy of actinide and cerium monpnictides was developed by Kasuya *et al.*<sup>99,100</sup> Their model allowed for the interaction between the p orbitals of the anion and the localized 5f electrons. They demonstrated that the interaction of the 5f states with holes in the valence band, formed by the p orbitals of the pnictogen, is of the Coulomb nature and in the second order of perturbation theory gives rise to a correction to the crystal field energy.

This mechanism is known as the p-f mixing effect and it is strongly anisotropic even in the case of the f ions in the cubic environment and it makes it possible to explain qualitatively many features of the magnetic behavior of cerium and light-actinide monopnictides.

A shortcoming of both these approaches in the explanation of the magnetism of actinide monocompounds is the fact that the Cooper and Kasuya models assume that the ground state is ionic, which does not agree with the available data on the electron structure of light-actinide monocompounds. The very fact that in the description of magnetic properties of these compounds one can use quite successfully either of these two theories, which begin with very different physical assumptions, shows that further refinement of the nature of the magnetic ordering of actinide monocompounds is still necessary.

A better understanding of the current situation in the study of the magnetism of actinide compounds can be obtained by analyzing, by way of example, our knowledge about the  $U_{1-x}Th_xSb$  pseudobinary system. Materials with compositions in the range  $x < 0.07$  exhibit a low-temperature antiferromagnetic ordering of the I type.<sup>54</sup> In the case of compositions with  $x > 0.25$  the magnetic ordering is ferromagnetic. In intermediate compositions  $0.07 < x < 0.25$  an incommensurate magnetic structure forms in the vicinity of the Néel temperature and transforms to a 3k structure of the IA type at low temperatures. An increase in the concentration of thorium lowers the magnetic ordering temperature which tends to zero at  $x \approx 0.8$ . It is interesting to note that the magnetic moment per uranium atom in this system does not

remain constant, but decreases on increase in the thorium concentration (Fig. 18). At present there are at least three models which can account for this unusual composition dependence of the magnetic moment of uranium.

One of these models<sup>101</sup> relates the reduction in the magnetic moment of uranium to the change in the state of the uranium ion from trivalent in USb to quadrivalent, as the concentration of thorium is increased to  $x_c \approx 0.3$ . Since the ground state of the  $U^{4+}$  ion is a nonmagnetic singlet, the magnetic moment of uranium in materials with high thorium concentrations is due to the mixing of higher levels with the ground state because of the exchange interaction. The dependence  $M_0(x)$  calculated in this model is represented by the dashed curve in Fig. 18a. The authors of Ref. 101 assumed that near the critical concentration  $x_c$  there may be a mixed-valence state.

A different explanation of the magnetic behavior of the  $U_{1-x}Th_xSb$  system is given in Refs. 89 and 102. This explanation is based on the data obtained by spin-polarization photoemission spectroscopy demonstrating that the moments of the 6d electrons are antiparallel to the 5f moments in light-actinide monocompounds. If, in agreement with the neutron-diffraction data, we assume that in USb the moment of the 5f electrons is  $\mu_f = 2.82 \mu_B$  and the moment contributed by each 6d electron is  $\mu_d = 1.3 \mu_B$  (which is the value obtained by comparing the experimental data with the formula given below), we can describe the dependence of the magnetic moment of uranium on  $x$  by the simple formula:

$$M_0 = \mu_f - \frac{x}{1-x} \mu_d. \quad (11)$$

It is assumed here that the rigid-band model applies to the 6d electrons. The theoretical dependence of the magnetic moment of uranium on the composition of  $U_{1-x}Th_xSb$  is represented by a chain curve in Fig. 18a.

It was pointed out in Ref. 80 that these two approaches are unsatisfactory and it was suggested that the change in the magnetic moment of uranium can be described by postulating that the strong p-f mixing which occurs in USb is suppressed on increase in the thorium concentration because of a reduction in the density of conduction electrons.

This example demonstrates the difficulties encountered in the interpretation of the magnetic phenomena in light-actinide compounds, which are usually attributed to the complexity of their electron structure originating mainly from the partial delocalization of the 5f electrons. However, it should be stressed that even actinide compounds in which the 5f electrons can be regarded as well-localized frequently have unusual magnetic properties.

One of such compounds is uranium dioxide  $UO_2$  which together with uranium monocompounds, has been investigated most thoroughly. Figure 19 shows, for the sake of comparison, the energy band structures of  $UO_2$  and USb obtained from an analysis of the optical spectra of these compounds.<sup>87,103</sup> We can see that the 5f electrons in  $UO_2$  are almost completely localized and that this compound is a magnetic semiconductor.

The transition from a paramagnetic to an antiferromagnetic state in  $UO_2$  at 31 K is a first-order phase transition,<sup>104,105</sup> although according to the Landau theory of phase transitions it can generally be a second-order transition.<sup>106</sup> The method of  $\epsilon$  expansion was used in Refs. 107–109 to

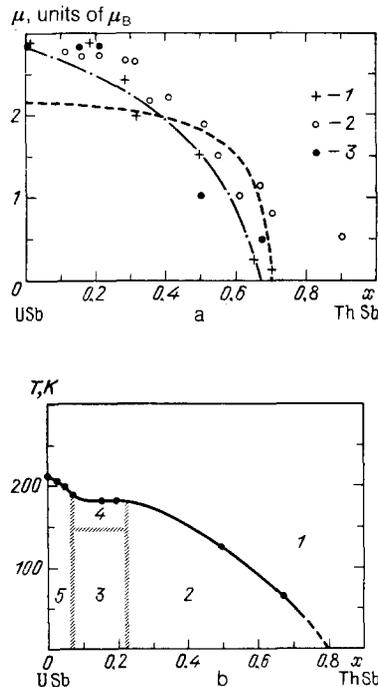


FIG. 18. Magnetic properties of the  $U_{1-x}Th_xSb$  system. a) Dependences of the atomic magnetic moment (per uranium atom) on the composition based on the following data: 1) measurements of the magnetization in low fields<sup>101</sup>; 2) measurements of the magnetization<sup>54</sup> at  $T = 4.2$  K in a magnetic field  $H = 100$  kOe; 3) neutron diffraction measurements.<sup>54</sup> The dashed and chain curves represent theoretical dependences.<sup>89,101,102</sup> b) Magnetic  $x$ - $T$  phase diagram: 1) paramagnetic phase; 2) ferromagnetic phase; 3) antiferromagnetic phase, 3k structure of type IA; 4) antiferromagnetic incommensurate phase; 5) antiferromagnetic phase, 3k structure of type I.

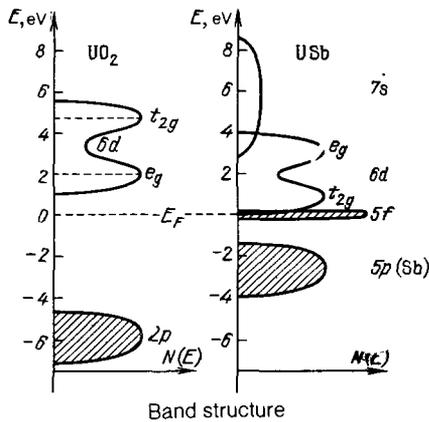


FIG. 19. Band structures of  $\text{UO}_2$  and  $\text{USb}$  (Ref. 87).

show theoretically that such an unusual situation is associated with the nature of critical fluctuations which, in turn, are governed by the magnetic structure of a crystal and by the nature of the spin-spin interactions. It is found that the appearance of a noncollinear antiferromagnetic  $3k$  structure of type I in  $\text{UO}_2$  is accompanied, as demonstrated by the neutron diffraction method, by a small ( $0.014 \text{ \AA}$ ) displacement of oxygen atoms from the positions they occupy in the paramagnetic state.<sup>110,111</sup> These displacements occur in such a way that the cubic symmetry of the crystal lattice of  $\text{UO}_2$  is retained also below the Néel temperature. A theoretical analysis of the microscopic mechanisms of an inhomogeneous (over a unit cell) modification of a crystal structure in which the latter apparently becomes "aligned" to the magnetic structure had led to the conclusion that an important role is played by the interaction of electric quadrupole moments of uranium atoms.<sup>112</sup> It is possible that an allowance for this interaction will be important also in the interpretation of the magnetic properties of light-actinide monocompounds discussed above.

## 8. CHARACTERISTICS OF CRITICAL BEHAVIOR AND MAGNETIC EXCITATIONS IN ACTINIDE COMPOUNDS

Important information on the characteristic features of the magnetic ordering of actinide compounds can be obtained by the neutron scattering methods. We shall consider briefly the results of experiments involving magnetic critical scattering and inelastic neutron scattering in actinide magnetic materials. The former method provides information on the critical behavior of the magnetic subsystem and can be used to study the anisotropy in regions characterized by a short-range magnetic order. The latter method gives information on magnetic excitations and, therefore, on various single-ion and ion-ion interactions.

Magnetic excitations and magnetic critical scattering have been investigated most thoroughly in uranium mononictides and monochalcogenides.

Investigations of the critical neutron scattering have been made on antiferromagnetic pnictides  $\text{UN}$  (Ref. 113),  $\text{USb}$  (Ref. 114), and  $\text{UAs}$  (Refs. 115 and 116). In the first two compounds the maxima of the critical scattering intensity occurred at the centers of the Brillouin zones corresponding to an antiferromagnetic structure of type I, which appears in these compounds below the Néel temperature  $T_N$ . In the case of  $\text{UAs}$  the strongest critical scattering is observed at points of the  $(1; 1; 0.3)$  type in reciprocal space,

which is evidence of the existence of magnetic fluctuations with a sinusoidal (and possibly incommensurate with the crystal lattice period) antiferromagnetic ordering. As pointed out already, in the case of  $\text{UAs}$  at  $T_N = 127 \text{ K}$  a first-order transition takes place from a paramagnetic state to an antiferromagnetic state with a collinear  $1k$  structure of type I. Therefore, the short-range order in the paramagnetic range of  $\text{UAs}$  differs from the long-range magnetic order that exists below the Néel temperature. The critical scattering in uranium mononictides is very strongly anisotropic, indicating the existence of quasitwo-dimensional fluctuation-induced regions of magnetic ordering with a correlation length which in  $(001)$ -type planes is several times longer than along directions perpendicular to these planes.

These features of the critical neutron scattering in uranium mononictides are in good agreement with the properties of these compounds observed in the magnetically ordered range (particularly those with a strong magnetic anisotropy) and can be described using the mean-field model with a Hamiltonian that includes the anisotropic exchange interaction and a strong (comparable with the exchange) cubic single-ion anisotropy. The critical behavior of uranium monoarsenide near the Néel temperature<sup>115,116</sup> is very similar to the behavior in the vicinity of what is known as the Lifshitz point where the paramagnetic and antiferromagnetic commensurate and incommensurate phases are in equilibrium. In the mean-field model this behavior is attributed to "frustration" because of the almost complete compensation of the antiferromagnetic interaction of the  $z$  components of the spins in nearest  $(001)$  planes and the ferromagnetic interaction of the same spin components lying in the second-nearest  $(001)$  planes. It is found that the interaction between the  $z$  components of the spins of atoms lying in the same  $(001)$  plane is approximately 40 times stronger than the exchange between the  $x$  and  $y$  components of the same spins.

The results of the experiments on inelastic neutron scattering in uranium monocompounds have not yet been finally interpreted. In the main, these results reduce to the following.

In the case of uranium antimonide there are two branches of magnetic excitations<sup>117</sup> with energy gaps of 6 and 27 meV at the point  $X$  in the Brillouin zone (Fig. 20). Several hypotheses have been put forward on the origin of these and other features found in the spectra of magnetic excitations of uranium antimonide. These hypotheses postu-

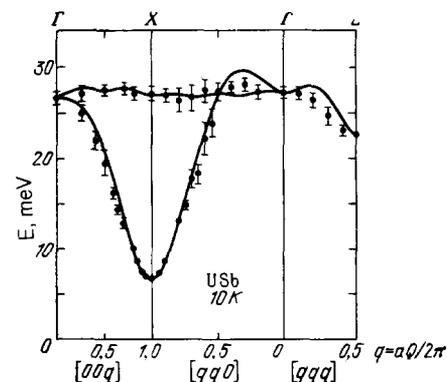


FIG. 20. Spectrum of magnetic excitations in  $\text{USb}$  at  $10 \text{ K}$  (Ref. 117). The symbols represent the experimental results and the curves are calculated in the random phase approximation using the model of localized  $5f$  electrons.

late the existence of the band magnetism of the 5f electrons,<sup>118</sup> mixed valence,<sup>119,120</sup> etc. However, a relatively complete description of such a spectrum of USb is given only in Refs. 117 and 121. This description, based on the random phase approximation and allowing only for the anisotropic bilinear exchange interaction and for the crystal field, is derived solely from the similarity of the spectra of magnetic excitations in USb and CeAs. The authors of these investigations conclude that the magnetic excitations observed in USb are transverse spin waves in the system of the localized 5f<sup>3</sup> electrons. It is important to note that in the case of a suitable selection of the parameters one can use this model to describe satisfactorily not only the pattern of magnetic excitations, but also other properties of USb (Néel temperature, antiferromagnetic 3k structure, etc.). The spectrum of magnetic excitations in UTe is qualitatively similar<sup>122</sup> to the spectrum of USb. There are grounds for assuming that it can also be described in the model of localized 5f electrons.

The nature of the inelastic magnetic neutron scattering in UN (Ref. 120), UAs (Ref. 52), and US (Ref. 123) differs qualitatively from the corresponding scattering in USb and UTe. This is not surprising because the crystal lattice parameters of USb and UTe are considerably larger (6.16 and 6.18 Å) and, consequently, the distances U-U are larger than in UN, UAs, and US (4.89, 5.78, and 5.49 Å, respectively). The last group of compounds does not exhibit generally the scattering corresponding to long-lived spin waves. For example, in the case of UN there is a wide intensity peak at the point (1, 1, 0) in the space of the wave vectors of the transferred momenta. The inelastic neutron scattering in UN, UAs, and US is similar to the scattering in some rare-earth materials with mixed valence, for example CePd<sub>3</sub>, alloys belonging to the Ce-Th system, etc.<sup>52</sup> However, there are at least two important differences between these groups of the 5f and 4f materials. The former are magnetically ordered and have relatively high Néel temperatures whereas the latter are frequently nonmagnetic. The other difference is that whereas the existence of the mixed valence in the 4f materials follows from the behavior of many of their physical properties, in the case of the 5f materials the situation is not as clear.

A qualitative explanation of the inelastic scattering in UX compounds in Ref. 123 is based on the Anderson model in which the f-d fluctuations with characteristic frequencies 1–10 THz are considered. These fluctuations in compounds with a small lattice constant can have a very wide spectrum, similar to that observed in UN, UAs, and US. An increase in the lattice constant converts these fluctuations to relatively long-lived collective spin excitations of the spin-wave type.

Although the magnitudes of the anisotropic interactions deduced from the inelastic neutron scattering are phenomenological parameters, they can provide a useful basis for identifying the nature of the microscopic mechanisms responsible for the anisotropy and phase transitions if they are combined with quantities deduced from investigations of the magnetic anisotropy of actinide compounds.

## 9. MAGNETIC ANISOTROPY AND MAGNETOELASTIC EFFECTS

Very little work has been done on the magnetic anisotropy of actinide compounds. Investigations of the anisotropy have been hindered by the fact that single crystals are not

available for the majority of actinide magnetic materials. Moreover, the anisotropy of many compounds is so strong that magnetic saturation along the difficult magnetization direction cannot be achieved in the attainable magnetic fields, so that accuracy of determinations of the magnetic anisotropy is low.

At present it is generally accepted that the magnetic anisotropy of actinide compounds is determined by the degree of localization of the 5f electrons. It is assumed that if the 5f electrons are in the collective state (itinerant), then the magnetic anisotropy is weak (as already pointed out in Sec. 6, in many investigations a weak magnetic anisotropy is used as one of the criteria of the band nature of the magnetism of actinide compounds). However, if the 5f electrons are localized, then—by analogy with rare-earth magnetic materials—it is assumed that the magnetic anisotropy of these compounds is strong and it is of single-ion nature, i.e., it is due to the interaction between the anisotropic cloud of the 5f electrons and the crystal field of the lattice. It is then assumed that because of the strong spin-orbit interaction the electron cloud is not deformed by rotating the magnetic moment (model of a “rigid” electron cloud). Moreover, in those cases when the f-d hybridization and the p-f mixing effects are strong, an important (and sometimes decisive) contribution to the magnetic anisotropy may come from anisotropic exchange interactions (see Sec. 7).

As pointed out already, a typical band actinide ferromagnetic compound is the intermetallic compound UCo<sub>5.3</sub> in which the 5f electrons of uranium are transferred to the 3d band of cobalt.<sup>64</sup> The uniaxial magnetic anisotropy constant of this compound is small: it is of the order of the anisotropy constant of metallic cobalt and its compounds with nonmagnetic yttrium.<sup>124</sup>

In the case of UCo<sub>5.3</sub> the 5f electrons are completely delocalized and they do not carry a magnetic moment. However, in those compounds in which the delocalization of the 5f electrons is strong, but the actinide retains at least a small magnetic moment, we can expect a strong magnetic anisotropy. This is true of the intermetallic compound UFe<sub>2</sub> (Refs. 125–127). As pointed out already, the magnetic moment of uranium in this ferromagnetic substance is small (0.03–0.06 μ<sub>B</sub>),<sup>128</sup> i.e., the 5f electrons of uranium in UFe<sub>2</sub> are almost completely delocalized. Consequently, it follows from simple considerations that the anisotropy of this compound should be weak. It would seem that measurements of the anisotropy confirm these predictions<sup>125</sup>: at 0 K the first cubic anisotropy constant of UFe<sub>2</sub> is K<sub>1</sub> = 8 × 10<sup>4</sup> erg/g. However, subsequent investigations have shown that the situation is more complex<sup>126,127</sup>: the weak experimentally determined magnetic anisotropy of UFe<sub>2</sub> is due to a “random” compensation of two large contributions to the magnetic anisotropy, one of which is positive and due to the undeformed lattice (K<sub>1</sub><sup>0</sup>) and the other is negative and due to the magnetoelastic interaction (ΔK<sub>1</sub><sup>me</sup>). These contributions are approximately equal in absolute value and they amount to 10 erg/cm<sup>3</sup>, i.e., they are two orders of magnitude higher than the measured anisotropy constant of UFe<sub>2</sub> (Refs. 126 and 127), shown in Fig. 21. We can assume that in this compound the localized part of the spin density of the 5f electrons is very strongly anisotropic. It should be pointed out that the situation in UFe<sub>2</sub> is qualitatively analogous to that

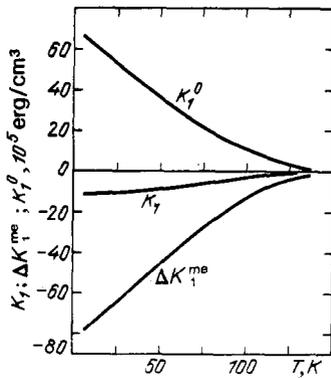


FIG. 21. Temperature dependences of the experimental values of the first magnetic anisotropy constant  $K_1$  of  $\text{UFe}_2$ , of the magnetoelastic contribution to the first anisotropy constant  $\Delta K_1^{\text{me}}$ , and of the anisotropy constant of the undeformed lattice  $K_1^0 = K_1 - \Delta K_1^{\text{me}}$  (Ref. 126).

in samarium iron garnet.<sup>129</sup> In this garnet the magnetic moment of  $\text{Sm}^{3+}$  is close to zero, since the spin component compensates almost completely the orbital component of the magnetic moment. On the other hand, since the orbital moment of  $\text{Sm}^{3+}$  differs from zero and interacts with the crystal field, the single-ion magnetic anisotropy due to samarium in this iron garnet is strong. Clearly, a considerable magnetic anisotropy discovered in the band ferromagnetic compound  $\text{UPt}$  (Ref. 130) can also be explained by partial delocalization of the 5f electrons.

The examples given above represent practically all the published data on the magnetic anisotropy of actinide compounds with collectivized or nearly collectivized (itinerant or near-itinerant) 5f electrons. Little more information is available on the magnetic anisotropy of actinide compounds in which the 5f electrons are regarded as largely localized.

The intermetallic  $\text{UGa}_2$  (with the hexagonal crystal structure of the  $\text{AlB}_2$  type)<sup>131,132</sup> is typical of this class of actinide magnetic materials. The easy magnetization axes are directions of the [100] type in the basal plane of the crystal and the difficult magnetization direction is parallel to the [001] hexagonal axis. In the investigated fields (up to 75 kOe) the magnetization along this direction does not exceed 0.1 of the saturation magnetization and estimates indicate that the uniaxial anisotropy field exceeds  $10^6$  Oe along the hexagonal axis, which corresponds to an effective magnetic anisotropy constant of  $2 \times 10^7$  erg/cm<sup>3</sup>.

Similar data have been reported for the orthorhombic compound  $\text{UGe}_2$  (Ref. 133), hexagonal compounds  $\text{UGaCo}$  and  $\text{UGaNi}$  (Ref. 134), tetragonal compounds  $\text{UAsS}$  and  $\text{UAsSe}$  (Ref. 135), cubic compounds  $\text{US}$  (Refs. 83 and 84),  $\text{USe}$  (Refs. 84 and 136), and  $\text{UTe}$  (Refs. 84 and 137). In the case of all these ferromagnetic materials the magnetic anisotropy fields exceed  $10^6$  Oe and the magnetic anisotropy energy is in excess of  $10^7$  erg/g.

In all the above examples of strong anisotropy its strength is known only to within an order of magnitude, since magnetic saturation along the difficult magnetization axis had not been achieved in the relevant experiments. At present there is only one actinide compound ( $\text{U}_3\text{As}_4$ ) with almost localized moments in which the characteristic features of the magnetization process has made it possible to achieve magnetic saturation along the difficult magnetiza-

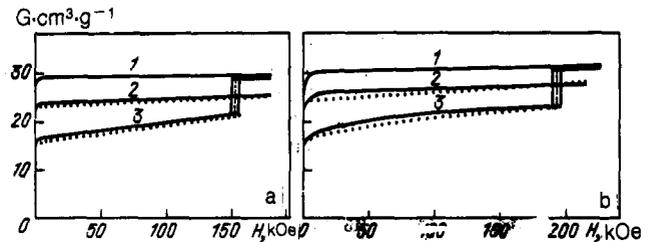


FIG. 22. Field dependences of the magnetization of a  $\text{U}_3\text{As}_4$  crystal along the following axes: 1) [111]; 2) [110]; 3) [100]. Temperature  $T$  (K): a) 77; b) 4.2. The results were taken from Ref. 140. The continuous curves are the experimental data and the dotted curves are calculated.

tion axis. Therefore, the magnetic anisotropy of this compound has been investigated more thoroughly. The magnetic ordering in  $\text{U}_3\text{As}_4$  (with the cubic structure of the  $\text{Th}_3\text{P}_4$  type) is ferromagnetic below 199 K (Ref. 138). The easy magnetization axes are directions of the [111] type and the magnetization along the difficult [100] axis reaches saturation abruptly in fields of the order of 100–200 kOe (Refs. 139–141), shown in Fig. 22. This type of field dependence of the magnetization can be explained allowing for two cubic anisotropy constants.<sup>140–143</sup> Calculations carried out within the framework of this model made it possible to determine the first  $K_1$  and second  $K_2$  magnetic anisotropy constants of  $\text{U}_3\text{As}_4$  at different temperatures<sup>140,141</sup> (Fig. 23). These calculations were made on the assumption that  $\text{U}_3\text{As}_4$  is a collinear ferromagnetic compound. In fact, the magnetic structure of this compound is noncollinear: it is formed by three sublattices whose magnetic moments lie in different planes of the (110) type at an angle to the [111] easy magnetization directions.<sup>144</sup> A theory of the magnetization of such structures is developed in Ref. 145. According to this theory the calculations carried out in the collinear model are valid also for a noncollinear structure if the distortions of such a structure in the field are slight and this is clearly true of  $\text{U}_3\text{As}_4$ .

The experimental data on the anisotropy of  $\text{U}_3\text{As}_4$  are in qualitative agreement with the calculations carried out in the single-ion model in the approximation of point charges.<sup>140</sup> However, estimates of the magnetic anisotropy<sup>146</sup> have demonstrated that the effective spin of uranium in  $\text{U}_3\text{As}_4$  is 3/2, whereas according to Ref. 145 the abrupt onset of the magnetization along the difficult axis is predicted by the single-ion model only for spins in excess of 3. Clearly, the contributions to the magnetic anisotropy of this compound include the single-ion mechanism and an important contribution of the p-f mixing mechanism discussed above.<sup>147</sup>

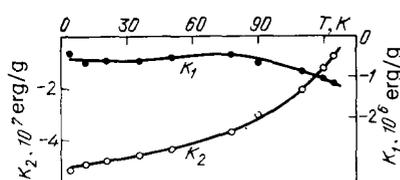


FIG. 23. Temperature dependences of the first  $K_1$  and second  $K_2$  magnetic anisotropy constants of  $\text{U}_3\text{As}_4$  (Ref. 140).

The strong magnetic anisotropy of actinide magnetic materials with the localized moments is responsible for a high coercivity of single crystals of these compounds when they are magnetized along the easy magnetization directions: at low temperatures the coercive force is 1–10 kOe. Figure 24 shows typical results obtained for UGaNi (Ref. 134) and similar data have been obtained for UAsSe (Ref. 148), UGa<sub>2</sub> (Ref. 131), USe (Refs. 84 and 136), and UTe (Ref. 137). This is due to the fact that in actinide compounds with almost-localized moments the magnetic anisotropy energy is comparable with the exchange energy and domain walls are thin: their thickness  $\delta$  represents only a few lattice parameters. A thin domain wall has an intrinsic coercivity

$$H_c = B \exp\left(-\frac{\pi\delta}{l}\right), \quad (12)$$

where  $B$  is a quantity of the order of the anisotropy field and  $l$  is the wavelength of the Peierls potential, which can be regarded as equal to the crystal lattice period.<sup>134</sup> A model of such thin domain walls is in good agreement also with the exponential fall of the coercive force on increase in temperature, which is exhibited by a number of actinide compounds (Refs. 84, 131, 134, 136, 137, and 148).

Rare-earth compounds exhibit a giant magnetostriction which is due to the interaction of the "rigid" undeformable cloud of the  $f$  electrons with the crystal field of the lattice (see, for example, the review in Ref. 149). As pointed out already, a similar model has been used in the interpretation of the data on the magnetic anisotropy of actinide compounds with localized  $5f$  electrons. Giant magnetoelastic strains, comparable with those observed in rare-earth compounds, can therefore be expected in the magnetically ordered states of magnetic materials of this type.

Few investigations have been made of the magnetostriction of actinide compounds in magnetic fields. Information on the magnetoelastic interaction in such magnetic materials can be obtained from x-ray diffraction measurements of distortions of the crystal structure below the magnetic ordering temperature. However, it should be pointed out that the crystal structure data cannot give the final information on the magnetoelastic interactions, because distortions of the crystal structure may be due to other factors, such as the Jahn-Teller effect. Therefore, the structure investigations should be checked and confirmed by magnetic methods.

The first measurements of the magnetostriction of actinide magnetic materials were carried out on the cubic compound U<sub>3</sub>P<sub>4</sub> (Ref. 150). Figure 25 gives the field dependences of the longitudinal magnetostriction of a single crystal of this compound determined along the [111] (a) and [110] (b) axes.<sup>150</sup>

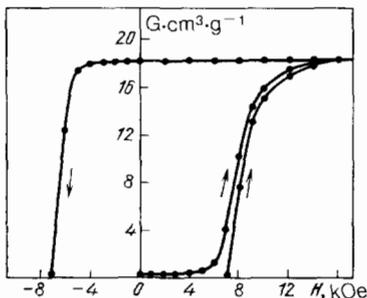


FIG. 24. Magnetization curve and hysteresis loop of UGaNi recorded at 4.2 K along the [001] direction.<sup>134</sup>

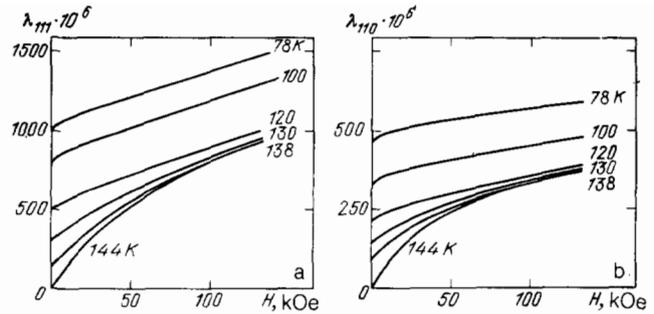


FIG. 25. Magnetic field dependences of the longitudinal magnetostriction of an U<sub>3</sub>P<sub>4</sub> single crystal along the [111] (a) and [110] (b) axes.<sup>150</sup>

ences of the longitudinal magnetostriction of a single crystal of this compound determined along the [111] and [110] axes. We can see that the magnetostriction is very strong (of the order of  $10^{-3}$  at 80 K) and it is comparable with the magnetostriction of rare-earth metals and compounds.

On transition to a magnetically ordered state the cubic crystal structure of U<sub>3</sub>P<sub>4</sub> experiences magnetoelastic rhombohedral distortions. The magnetostriction constant  $\lambda_{111}$  determined by x-ray diffraction measurements<sup>151</sup> is in good agreement with the constant deduced from investigations of the field dependence of the magnetostriction.

A similar comparison of the magnetostriction and x-ray diffraction measurements has been made in the case of the isostructural compound U<sub>3</sub>As<sub>4</sub> (Ref. 152). In the case of this compound the magnetostriction constant  $\lambda_{111}$  exceeds  $10^{-3}$  at helium temperatures.

An enormous magnetostriction in the basal plane was also deduced from the magnetostriction and x-ray investigations of the hexagonal intermetallic UGa<sub>2</sub> (Refs. 131, 132, and 153). The values of the magnetostriction constant  $\lambda^{12}$  determined by various methods are in good agreement with one another.

These examples represent all the published information on the giant magnetostriction of actinide compounds deduced from measurements in magnetic fields. The data on the magnetostriction of other uranium, neptunium, and plutonium compounds reported briefly below were deduced from x-ray and neutron diffraction measurements of distortions of the crystal structure.

These results indicate that enormous magnetoelastic continuous anisotropic strains, exceeding considerably  $10^{-3}$ , appear in uranium monocompounds US, USe, UN (Refs. 154 and 155), UTe, UTe<sub>x</sub>Sb<sub>1-x</sub> (Ref. 156), neptunium compounds NpN and NpC (Refs. 47 and 157), and plutonium compound PuP (Ref. 158) all with the rocksalt structure, as well as in cubic Laves phases NpNi<sub>2</sub> and NpFe<sub>2</sub> (Ref. 158). The strongest distortion of the crystal lattice is found in NpFe<sub>2</sub>. It corresponds to the magnetostriction constant  $\lambda_{111} = -8 \times 10^{-3}$ .

We have discussed so far the magnetoelastic distortions of ferromagnetically ordered actinide compounds. X-ray and neutron diffraction investigations<sup>47,157</sup> of some antiferromagnetic actinide compounds have shown that their magnetoelastic properties depend on the nature of the magnetic structure. In compounds with the collinear 1k structures the magnetoelastic distortions of the crystal lattice are usually

very strong (of the order of  $10^{-3}$ ). However, in the case of those compounds which have complex noncollinear high-symmetry magnetic structures (multi-k structures, structures of the spin-wave type, etc.), the magnetoelastic distortions are weaker (less than  $10^{-4}$ ). This is manifested most clearly in the case when variation of temperature alters the nature of magnetic ordering. For example, NpAs has the rocksalt structure in the paramagnetic state. Below the Néel point, which is 172.5 K, the structure of NpAs is collinear antiferromagnetic of type I and the appearance of this structure is accompanied by tetragonal distortions of the crystal lattice. At a temperature of about 140 K there is a transition to an antiferromagnetic phase of the spin-wave type and distortions of the cubic lattice disappear.

The reason for such a strong influence of the nature of the antiferromagnetic structure on the magnetoelastic distortions is not yet fully understood. In some cases the absence of distortions of the crystal structure is due to the appearance of noncollinear multi-k structures, whose symmetry forbids the appearance of anisotropic magnetostrictive strains.

We discussed above the magnetoelastic phenomena in those actinide compounds whose properties can be described by the model of localized or almost-localized 5f electrons. There is practically no published information on the magnetostriction of actinide compounds with the band magnetism. If we use simple ideas on the magnetism of collective-state (itinerant) electrons, we then find that anisotropic magnetoelastic strains in band magnetic materials should be weak. However, investigations of magnetoelastic properties of the compound  $UFe_2$  in which the 5f electrons of uranium are almost all in the collective (itinerant) state, as mentioned above, demonstrate that the situation is not so simple. Giant or rhombohedral distortions of the crystal structure appear in this compound below the Curie point.<sup>126</sup> These distortions, like the strong anisotropy of the undeformed lattice of  $UFe_2$ , are clearly due to the existence of a small localized component of the magnetic moment of uranium.

## 10. CONCLUSIONS

We can see from this review that in the 35 years since the discovery of the strong magnetism of actinide compounds an enormous amount of experimental data on their magnetic properties has been accumulated. It has been found that many actinide magnetic materials have unusual magnetic properties which are not encountered in materials based on the 3d transition and rare-earth elements.

The situation is much less satisfactory in respect of theoretical interpretation of the experimental data. In most cases the magnetism of actinides is discussed using rough alternative concepts of total localization or total delocalization of carriers of magnetism. Even in the case of the most thoroughly investigated groups of actinide compounds such as monochalcogenides and mononpnictides, which can be described by more refined models allowing for the possibility of partial localization (or collectivization) of the 5f electrons as a result of their interaction with other groups of electrons, an analysis is made at the qualitative level or at best at the semiquantitative level, and it is found that the experimental data can be described equally well by models based on basically different physical assumptions.

This situation has arisen because, on the one hand, the

experimental investigations have often been limited to the main characteristics of actinide magnetic materials and have been carried out on compounds belonging to the first half of the actinide series (up to plutonium and sometimes up to americium). The magnetic properties of compounds of heavy actinides (californium, einsteinium, etc.) have not yet been investigated.

On the other hand, difficulties encountered in the theoretical interpretation of the properties of actinide magnetic materials are related to the complexity and insufficient knowledge of their electron structure.

In our opinion, the following experimental and theoretical investigations of the actinide magnetism are the most urgent:

- 1) determination of the magnetic structures and other properties of heavy actinide metals and their compounds;
- 2) experimental and theoretical studies of the Mott transition and of the associated phenomena in the 5f-electron system of actinide magnetic materials;
- 3) development of a theory and experimental studies of the band magnetism of the 5f electrons;
- 4) identification of microscopic mechanisms of the exchange and other interactions in actinide compounds.

Bearing in mind the complexity of the systems with the 5f electrons, it is necessary to tackle these tasks by applying a wide range of experimental methods including not only the "classical" magnetic techniques, but also the methods from nuclear physics, optical and x-ray spectroscopy, studies of transport effects, etc.

The authors are grateful to K. P. Belov and V. I. Ozhgin for their encouragement.

<sup>11</sup>An increase in the susceptibility of americium at low temperatures is in all probability due to the presence of heavy actinide impurities and/or the influence of defects which appear as a result of radioactive decay. It would be of interest to carry out experimental investigations of this topic.

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