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Systematics in the Magnetic Properties of Ternary Actinoid Oxides

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Magnetic data for ternary actinoid oxides with central ions exhibiting the [Rn]$5f^n$ electronic structure have been investigated to establish systematics for magnetic behavior and/or relations between structure and magnetism. All compounds with [Rn]$5f^0$ central ions exhibit a temperature-independent susceptibility which is ascribed to ligand orbital admixture into the $5f$ orbitals. The magnetic moments of [Rn]$5f^1$ compounds are composed of a constant and a temperature dependent part, which are ascribed to ligand orbital admixtures and the $5f$ electrons, respectively. The low temperature behavior of [Rn]$5f^{2n+1}$ compounds can be qualitatively explained by the lattice structures involved: *An*–O–*An* chains are necessary to make superexchange possible and a certain maximum distance between the paramagnetic ions must not be exceeded.

1. Introduction

The first magnetic investigations on ternary oxides of the actinoids took place in the fifties and sixties (*1*, *2*). While at that time there were still discussions about the origin of magnetic moments from $6d$ or $5f$ electrons, there is nowadays no more doubt concerning the role of the $5f$ shell with respect to actinoid magnetism. However, in contrast to the $3d$ transition metals which obey the L–S coupling scheme with spin–orbit (SO) and Zeeman splittings small in comparison with crystal field (CF) splitting, and in contrast to the lanthanoids with a strongly dominating SO splitting, the actinoid series electronic behavior is more complicated. Here the CF splittings usually lie between those of the lanthanoids and the d transition metals; in addition, the respective multiplet splittings lie in the same energy range. The dominant reason for these facts lies in the larger spatial extent, and therefore reduced shielding, of the $5f$ compared to the $4f$ orbitals.

One important consequence of these facts is the variation in the lighter actinoids of oxidation states between +3 and +7; another is the magnetic behavior of actinoid compounds. In Figs. 1 and 2 the experimental magnetic moments of lanthanoid and actinoid compounds (*3*), respectively, are plotted against the number of electrons in the respective f shell. The full and dotted lines in the diagrams correspond to the theoretical values of the free ions, without and with inclusion of the Van Vleck temperature independent paramagnetism (TIP), respectively (the calculation of the free ion paramagnetic moments was carried out according to (*27*)). It is obvious that the agreement between theoretical and experimental values is very good in the case of the lanthanoids but rather unsatisfactory in the case of the lighter actinoids.

These findings can be explained by the stronger influence of crystal fields on the more extended $5f$ orbitals and by a higher degree of covalent bonding in these compounds. This covalency manifests itself in

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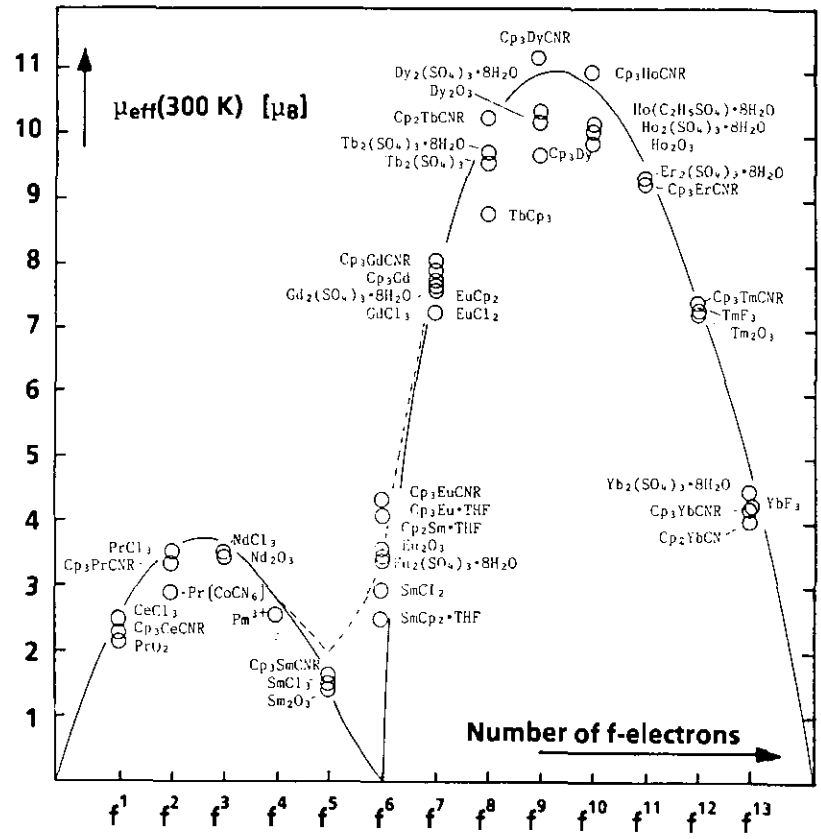

FIG. 1. Magnetic moments of lanthanoid ions in comparison with theoretical values. The dotted line includes the Van Vleck TIP in the calculation (*3*).

the fact, that an appropriate description of the $5f$ electron behavior requires, even in the $5f^1$ case (no electronic repulsion), not only the SO coupling constant ζ and the crystal field parameters Δ and Θ, but also the two orbital reduction factors k and k' to account for the reduction of orbital moments due to covalency effects (*4–6*). Concerning magnetic properties, these effects generally lead to a reduction of the magnetic moments in comparison with theoretical ones.

Over the last 20 years attention to systematics of magnetic behavior has been focused principally on actinoid metals, binary oxides, monopnictides, and chalcogenides; information on ternary oxides is much more fragmentary (*4, 7–13*). In recent years we investigated ternary oxides of the actinoids, concentrating on the [Rn]$5f^0$ and [Rn]$5f^1$ electronic configurations as the simplest cases, mainly directed towards U(VI) and Np(VI) ions (*14–21*). Ternary oxides of neptunium are well known; most of them are isostructural with the corresponding uranium compounds. Furthermore, ^{237}Np allows direct insight by Mössbauer spectroscopy into electric and magnetic forces acting at the neptunium site in the lattice.

In particular we were interested in relationships between magnetism and lattice structure in these compounds, because

—coordination to a great extent determines the magnetic moment and

—lattice structure properties are important criteria for the possibility of magnetic ordering at low temperatures.

Magnetic ordering has already been observed in several ternary actinoid oxides (*4, 6–13, 28*); however, due to the paucity of

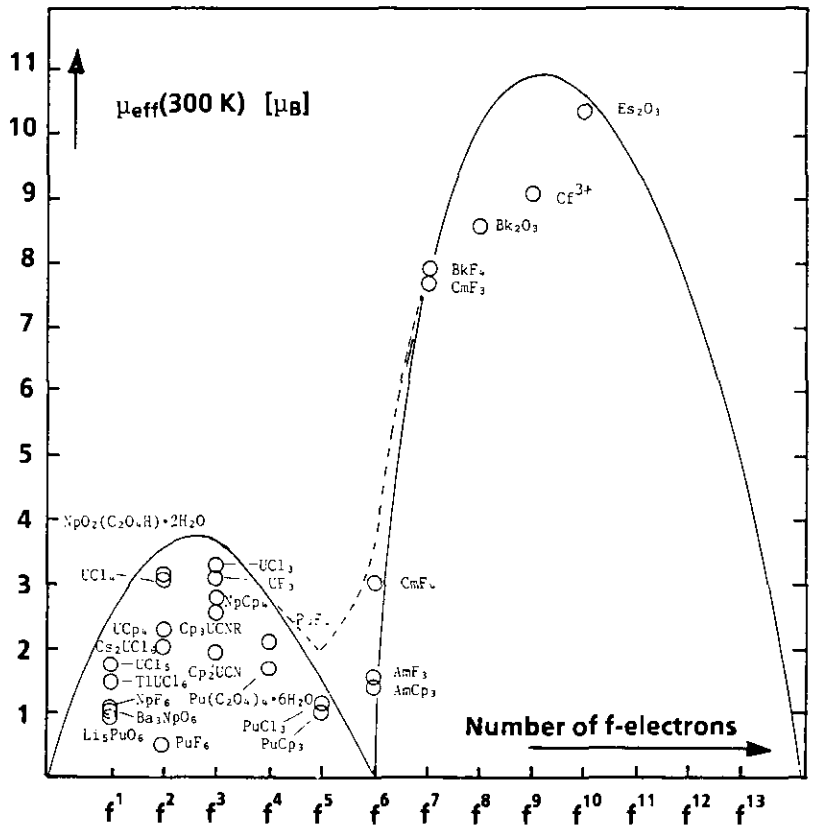

FIG. 2. Magnetic moments of actinoid ions in comparison with theoretical values. The dotted line includes the Van Vleck TIP in the calculation (*3*).

compounds investigated no systematics had been suggested in contrast to, e.g., the monopnictides (*29, 30*).

Magnetic ordering phenomena at low temperatures are expected in ternary actinoid oxides with odd numbers of *f* electrons, due to their magnetic ground states. This ordering could be due to dipole–dipole interactions (DDI) or exchange interactions. The DDI is a long range interaction with small interaction energies. As an example, for a magnetic moment of $1\mu_B$ and a distance of 300 pm the dipole field is approximately 0.07 T, corresponding to an interaction energy of 5×10^{-2} K. Total energies usually lie below 1 K; hence, magnetic ordering due to DDI only occurs at very low temperatures. Therefore, exchange interactions must be the origin of magnetic ordering in ternary oxides.

Since direct exchange can only appear when the ions are in proximity and their electronic orbitals overlap, which is not the case in the compounds studied, superexchange must be responsible for the observed ordering phenomena. The possibility of superexchange, however, depends strongly on the lattice structure. Therefore, some systematic relations are anticipated between structure and magnetism in these compounds.

The purpose of this work is to gather and compile magnetic data on the hitherto investigated ternary actinoid oxides, to explain in a qualitative manner the high-temperature magnetism of the $[Rn]5f^0$ and $[Rn]5f^1$ systems, and to develop some systematics for the magnetic properties of systems with magnetic ground states.

Many of the data originate from papers

TABLE I

MAGNETIC SUSCEPTIBILITIES OF THE [Rn]$5f^0$ SYSTEMS IN 10^{-6} cm^3 mol^{-1}

Compound	χ^{dia}	Reference
α-Na_2UO_4	152	(*22*)
β-Na_2UO_4	114	(*22*)
Li_2UO_4	240[a]	(*22*)
β-Na_4UO_5	142	(*22*)
$Li_2U_2O_7$	135	(*23*)
$Na_2U_2O_7$	133	(*23*)
Sr_3UO_6	158	(*21*)
Ca_3UO_6	156	(*21*)
$BaUO_4$	134	(*18*)
$SrUO_4$	143	(*19*)
Na_4UO_5	162	(*20*)
Li_5NpO_6	225	(*22*)
Li_5NpO_6	217	(*14, 15*)

[a] The anomalously high susceptibility of Li_2UO_4 was explained by a ferromagnetic impurity present in the sample.

dealing with specific classes of compounds. Some, however, are so far available only in Institute reports in the German language. In addition, to the authors' knowledge, no article exists in which all the structural and magnetic properties of this class of compounds are collected, and in which the systematic relations are properly described.

This work is to be seen as a collection of experimental data: throughout, only measured values are related to each other. Of course, there are ways of calculating, or at least estimating, e.g., covalency fractions or exchange integrals. However, in most cases specific approximations and/or simplifications are necessary. Such calculations are not within the scope of this work: our goal is to stimulate interested theoreticians to quantify our qualitative findings with their own models.

2. The [Rn]$5f^0$ systems

All compounds hitherto investigated with a [Rn]$5f^0$ electronic configuration of the central ion exhibit a weak, temperature-independent, paramagnetic susceptibility (Table I).

In contrast to the results of Brochu and Lucas (*24*) the susceptibilities are independent of temperature over the whole range investigated (77–300 K), as should be expected from ions not containing any open electronic shells. Hence, it is suspected that the compounds reported in (*24*) contained paramagnetic impurities, perhaps U(V) or iron. An exception is $SrUO_4$, which contains U(V) intrinsically, since it exists only as the slightly substoichiometric material $SrUO_{3.991}$ (*19*).

The [Rn]$5f^0$ ions have no f electrons to generate a paramagnetic susceptibility. Hence, the existence of paramagnetism in these compounds is a clear sign for a certain degree of covalency present in the An–O bonds; i.e., the ternary oxides of U(VI) and Np(VII) cannot be considered as purely ionic. Since no electrons are available in the $5f$ shell, the observed susceptibility must be due to a mixing of ligand orbitals into the $5f$ electronic states.

This covalency is not surprising when actinyl groups are a feature of the crystal lattice, but even in compounds with six almost equidistant oxygen ions in the coordination octahedron the susceptibility lies in the same range. Thus, the influence of bonding electrons on the magnetic properties is not negligible in such systems.

The susceptibilities of the Np(VII) compounds are higher than those of the U(VI) compounds, which is consistent with the increasing tendency toward covalency with increasing oxidation state in the actinoid series.

3. The [Rn]$5f^1$ Systems

The common feature of all ternary oxides with a [Rn]$5f^1$ ion hitherto investigated is the presence of more or less distorted AnO_6 octahedra within the crystal lattice. The octahedra can be isolated or form a one, two, or three dimensional network. The respective unit cells and those of some $5f^3$ systems are displayed in Fig. 3 (*14*).

The presence and the distortions of these

AnO_6 octahedra have been established by X-ray and/or neutron diffraction, in addition to absorption spectroscopy in the near to far infrared energy range (*4, 7–22*).

The electronic configuration $5f^1$ exhibits a $^2F_{5/2}$ ground state and a $^2F_{7/2}$ first excited state (SO interaction). In an octahedral crystal field the $^2F_{5/2}$ is split into a Γ_7 and a Γ_8, the $^2F_{7/2}$ into a Γ_6, and Γ_8, and a Γ_7 state, as indicated in Fig. 4. The energy differences between the various levels depend on the ratio of the respective crystal field parameters. The Γ_7 always forms the ground state, even in a strongly tetragonally distorted octahedron, where a splitting scheme according to Fig. 5 would be observed.

The energies of the $\Gamma_7 \rightarrow \Gamma_8$ ($\Gamma_7 \rightarrow \Gamma_7'$) transitions lie in the range 4000 to 8000 cm^{-1}, compared with $kT = 203$ cm^{-1} at room temperature. From these values a population ratio of $\leq 2 \times 10^{-9}$ between the the ground state and the first excited state results. Thus only the ground state is significantly populated at room temperature. Hence, on first approximation one would expect the magnetic moment of an Γ_7 level, i.e., 1.24 μ_B, in these compounds.

From Table II it is obvious that none of the compounds investigated reaches this value. In all these ternary oxides the magnetic moments are lower, sometimes slightly, sometimes significantly, than the theoretical one. As mentioned above, this effect can be taken as indicating a significant degree of covalency in the *An*–O bonds; i.e., one cannot consider these compounds as purely ionic. This is not surprising, since the $5f^0$ actinoid ternary oxides already exhibit a certain degree of covalency, as has been stated above. This is manifested by an observable temperature-independent paramagnetic susceptibility. Indeed, this kind of TIP susceptibility also exists in the $5f^1$ compounds, as can be seen from Table III.

It is tempting to try to use the Van Vleck scheme for these observations in a manner analogous to the 4*f* compounds; however, in the present case the argument is insufficient. The optical experiments show that a significant population of higher electronic states cannot occur at room temperature (see above). Hence, the more probable explanation lies in the influence of the neighboring anions on the actinoid ion, which admixes different *J* multiplets into the ground state, or may even cause 5*f* orbital participation in bonding.

From the above discussion one would expect a correlation between magnetic moments and temperature-independent susceptibilities in this class of compounds, since both are influenced by the same effects, namely crystal field and covalency interactions. This correlation is indeed present, as can be seen in Fig. 6a and 6b, where the room temperature moments are plotted versus χ^{TIP} for the compounds listed in Tables II and III. Regression analysis yields a correlation coefficient of $r = 0.91$; i.e., a strong correlation exists. A regression line can be drawn through the data points to yield an intercept at $\mu_{res} = 0.49$ μ_B.

This value would correspond to a residual magnetic moment after elimination of the effects of ligand electrons, i.e., the "pure" moment of the $5f^1$ ion in its octahedral or quasioctahedral crystal field. If this were the case, the same value of μ_{res} should be obtained when the appropriate data of each compound were used in the following relation:

$$\mu_{res} = [(\chi(RT) - \chi^{TIP}) \cdot T \cdot 3k/N_L]^{1/2}.$$

This formula corresponds to the usual manner of calculating effective moments from susceptibilities, in which the temperature independent portion χ^{TIP} is eliminated. The results are plotted in Fig. 7. Obviously, the moments of the compounds no longer depend on χ^{TIP}, but scatter around a mean value, of $\mu_{res} = 0.51 \pm 0.16$ μ_B (2 s). All of the data points lie in the interval 0.51 ± 0.16 μ_B, 66% in the interval 0.51 ± 0.08 μ_B. The mean value obtained by this method is in excellent agreement with 0.49 μ_B obtained as intercept of the correlation line. While the scatter of points is relatively high, one must take into account the significant differ-

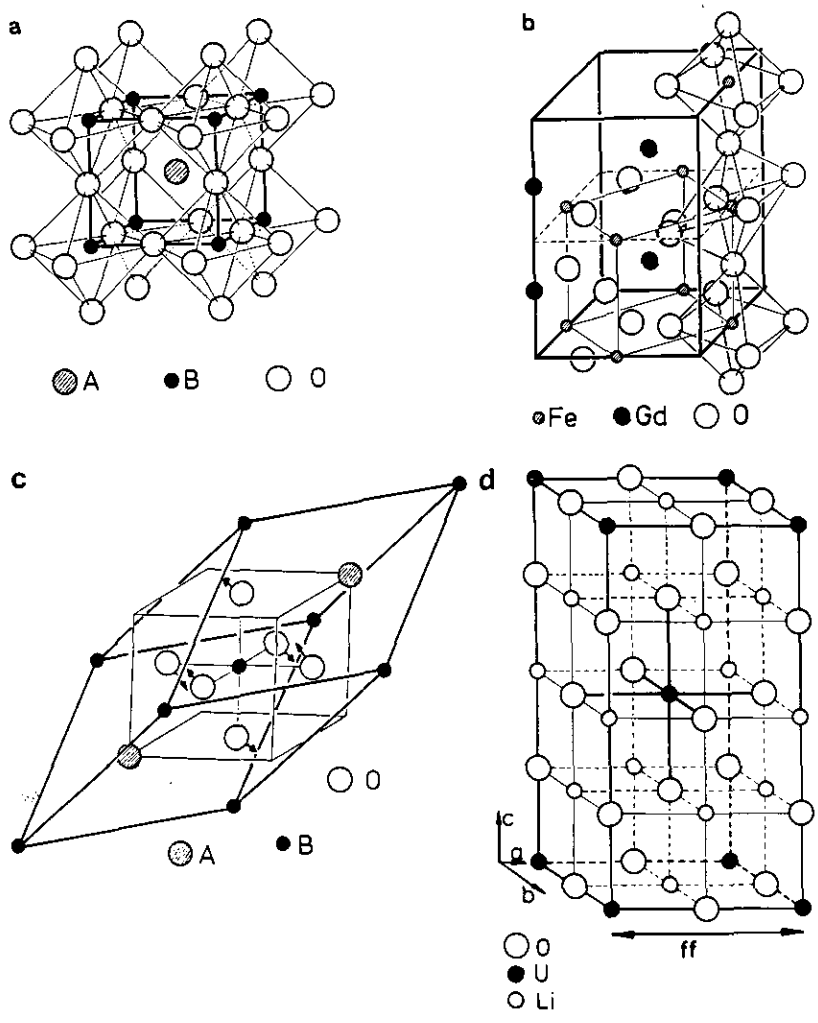

FIG. 3. Structures of some ternary oxides of the actinoids: (a) perovskite structure (KUO_3, $RbUO_3$); (b) $GdFeO_3$ structure ($NaUO_3$, $BaNpO_3$, $SrNpO_3$); (c) $LaAlO_3$ structure ($LiUO_3$); (d) Li_3UO_4; (e) Li_7UO_6, Na_6NpO_6, Li_6NpO_6, Li_5PuO_6; (f) Na_2NpO_4; (g) Li_4NpO_5, Na_4NpO_5; (h) M_3NpO_6; (i) $BaNpO_4$, $BaUO_4$, $SrUO_4$; (k) K_2NpO_4; (l) $NpGeO_4$.

ences between the individual crystal structures of the compounds, so that one cannot expect all oxides to exhibit exactly the same value.

As a conclusion of the above discussion the following statements can be made:

—The *An*–O bonds in ternary actinoid oxides exhibit a significant degree of covalency.

—The magnetic moments of these compounds seem to involve a constant and a variable part, the latter being determined by the degree of mixing of higher electronic states, probably from ligand atoms, into the ground state. The former should correspond to the moment of the pure Γ_7 crystal field state, but is quenched, possibly due to the effect of *f*-electron participation in bonding.

4. Low-Temperature Magnetism

Compounds having a magnetic ground state are expected to exhibit magnetic ordering at low temperatures.

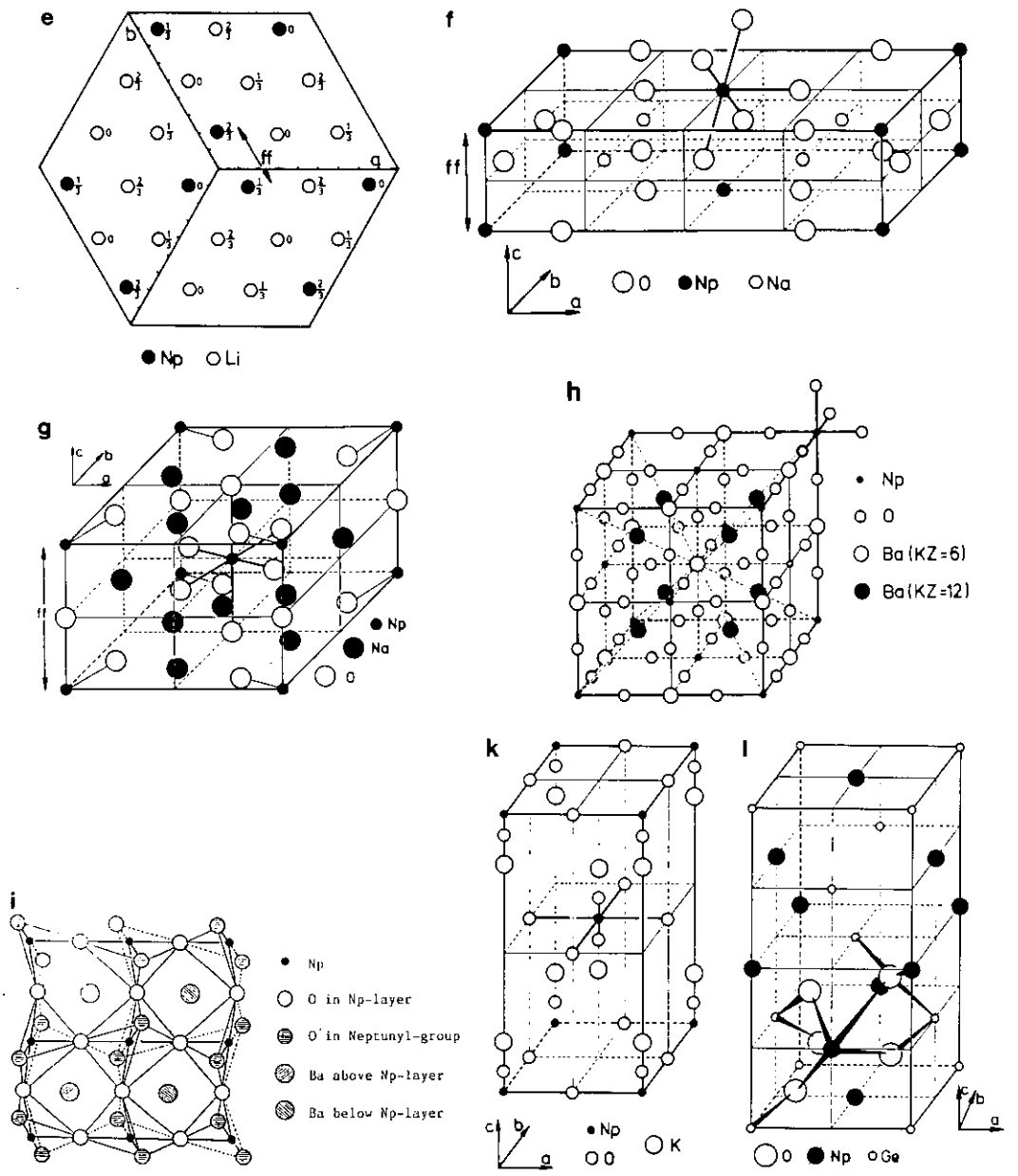

FIG. 3.—*Continued*

In Table IV all ternary oxides with a $5f^{2n+1}$ electronic configuration of the central ion investigated so far are listed with their lattice symmetry, their shortest *An–An* distance in the lattice, and their transition temperatures, if observed. The *An–An* distances (*ff*) have been calculated from the crystal structure using all available literature data (*14*), and the ionic radii given by Shannon (*25*).

For several of these compounds information on the kind of ordering, i.e., ferro- or antiferromagnetic, is available. However, in many cases this was not provided or could not be determined; furthermore, in a few cases discrepancies occur in the literature.

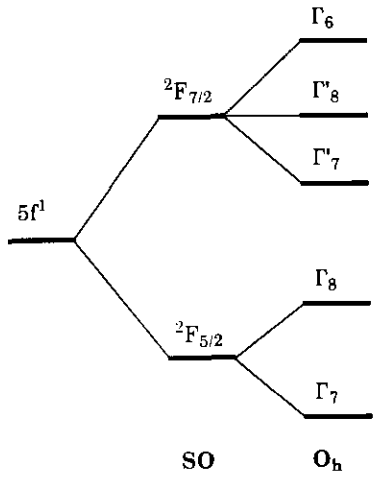

FIG. 4. Spin–orbit and crystal field splitting in an octahedral field.

In this paper that question is omitted, since for a qualitative discussion only the presence and the strength (as indicated by ordering temperature) of magnetic interaction are being studied.

The distances between the actinide central ions lie in the range from 300 to 700 pm.

TABLE II

MAGNETIC MOMENTS AT ROOM TEMPERATURE OF BINARY OXIDES WITH A $[Rn]5f^1$ CENTRAL ION

Compound	μ (μ_B)	Reference
$LiUO_3$	1.117	(*4*, *22*)
$NaUO_3$	1.125	(*4*, *22*)
KUO_3	1.216	(*4*, *22*)
$RbUO_3$	1.216[a]	(*7*)
Li_3UO_4	0.922	(*4*, *22*)
Li_7UO_6	0.873	(*4*, *22*)
Na_2NpO_4	1.053	(*4*, *22*)
Li_4NpO_5	0.994	(*4*, *22*)
Na_4NpO_5	1.018	(*14*, *20*)
Li_6NpO_6	1.083	(*14*, *15*)
Na_6NpO_6	1.005	(*14*)
Ba_3NpO_6	1.012	(*4*, *22*)
Sr_3NpO_6	0.933	(*21*)
Ca_3NpO_6	1.089	(*21*)
$BaNpO_4$	1.089	(*18*)
Li_5PuO_6	0.955	(*4*, *22*)

[a] Estimated from graph.

From the above model calculation and the magnitude of the magnetic involved it is clear that only a superexchange mechanism can be the cause of magnetic ordering.

The first condition for a superexchange

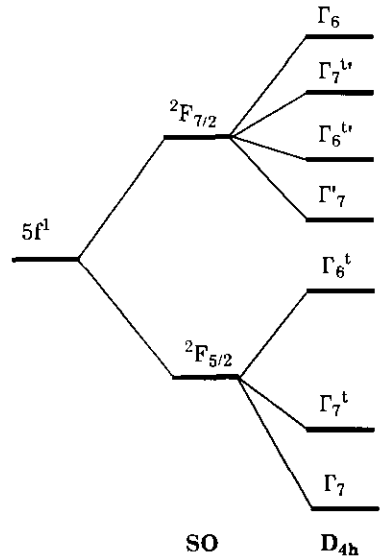

FIG. 5. Spin–orbit and crystal field splitting in a tetragonally distorted octahedral field.

TABLE III

TEMPERATURE-INDEPENDENT PARTS OF THE MAGNETIC SUSCEPTIBILITY IN TERNARY OXIDES WITH A $[Rn]5f^1$ CENTRAL ION IN 10^{-6} cm^3 mol^{-1}

Compound	χ_m^{TIP}	Reference
$LiUO_3$	364	(*4*, *22*)
$NaUO_3$	395	(*4*, *22*)
KUO_3	440	(*4*, *22*)
Li_3UO_4	280	(*4*, *22*)
Li_7UO_6	238	(*4*, *22*)
Na_2NpO_4	372	(*4*, *22*)
Li_4NpO_5	331	(*4*, *22*)
Na_4NpO_5	342	(*14*, *20*)
Li_6NpO_6	389	(*14*, *15*)
Na_6NpO_6	376	(*14*)
Ba_3NpO_6	340	(*4*, *22*)
Sr_3NpO_6	283	(*21*)
Ca_3NpO_6	347	(*21*)
$BaNpO_4$	335	(*18*)
Li_5PuO_6	300	(*4*, *22*)

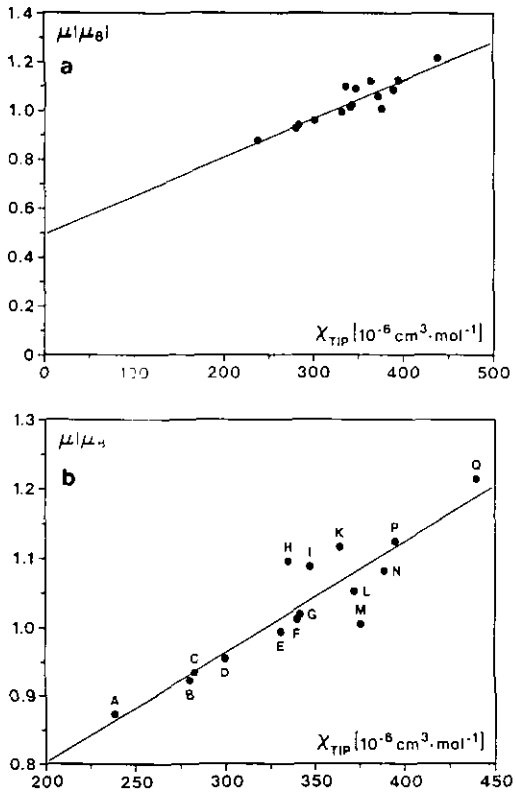

FIG. 6. Magnetic moments plotted versus TIP susceptibilities: (a) total, (b) zoomed.A: Li_7UO_6; B: Li_3UO_4; C: Sr_3NpO_6; D: Li_5PuO_6; E: Li_4NpO_5; F: Ba_3NpO_6; G: Na_4NpO_5; H: $BaNpO_4$; I: Ca_3NpO_6; K: $LiUO_3$; L: Na_2NpO_6; M: Na_6NpO_6; N: Li_6NpO_6; P: $NaUO_3$; Q: KUO_3.

ordering mechanism is the existence of either linear or bent *An*–O–*An* chains in the crystal lattice. Compounds which do not exhibit this configuration do not order magnetically.

Examples are provided by the alkaline orthoneptunates Li_6NpO_6 and Na_6NpO_6, or the uranate Li_7UO_6. The AnO_6 octahedra in their lattices are completely isolated; hence, no low temperature ordering is observed.

Even more striking is the example of the alkaline earth orthoneptunates. Their lattices contain chains of the type

$$-Np-O-M^{2+}-O-Np-,$$

M^{2+} being a (diamagnetic) alkaline earth ion. Here, the AnO_6 octahedra are completely isolated. If the diamagnetic ions are exchanged with paramagnetic ones this "isolation" is removed and the resulting compounds order magnetically at relatively high temperatures, as observed, for instance, in Ba_2MnNpO_6 or Ba_2FeNpO_6 (*14, 21, 26*).

It matters very little whether these *An*–O–*An* chains are present in one, two, or three lattice directions. Magnetic ordering is observed in, e.g., Li_4NpO_5 (one-dimensional chains), $BaNpO_4$ (two-dimensional chains), and KUO_3 (three-dimensional chains).

A strong influence, on the other hand, is exerted by the interactinoid distances in the lattice, as can be seen in Fig. 8. Here, a plot is presented of the observed transition temperatures versus the respective *An*–*An* distance in the lattice.

A "region of magnetic ordering" is delineated by two lines in this diagram. Slight changes to this region might occur upon the availability of new data; however, the general shape and also the critical point on the abscissa are not expected to change drastically. In addition, although this paper deals with pure oxides only, some mixed oxygen/halogen compounds such as UOCl, UOBr, and UOJ (*31*) would also fit in this scheme.

In all compounds with a linear –*An*–O–*An*– configuration magnetic ordering is observed below a certain critical dis-

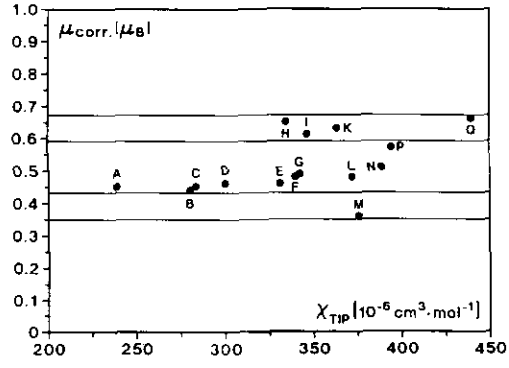

FIG. 7. Corrected magnetic moments plotted versus TIP susceptibilities; letters as in Fig. 7.

TABLE IV

TERNARY OXIDES INVESTIGATED SO FAR: THEIR CRYSTAL SYMMETRIES, An–An DISTANCES, AND TRANSITION TEMPERATURES

Electron configuration	Compound	Crystal symmetry	Shortest An–An distance (pm)	Transition temperature (K)
$5f^1$:	$LiUO_3$	rhombohedral	400	16.9
	$NaUO_3$	orthorhombic	413	31.1
	KUO_3	cubic	429	16.0
	$RbUO_3$	cubic	432	32.0
	Li_3UO_4	tetragonal	449	6
	Li_7UO_6	hexagonal	615	[a]
	Na_2NpO_4	orthorhombic	444	7
	K_2NpO_4	tetragonal	423	19.5
	Li_4NpO_5	tetragonal	443	20
	Na_4NpO_5	tetragonal	459	[a]
	Li_6NpO_6	hexagonal	520	[a]
	Na_6NpO_6	hexagonal	567	[a]
	Ba_3NpO_3	orthorhombic	627	[a]
	Sr_3NpO_6	orthorhombic	598	[a]
	Ca_3NpO_6	orthorhombic	574	[a]
	$BaNpO_4$	orthorhombic	404	18.3
$5f^3$:	$BaNpO_3$	rhombohedral	438	48.3
	$SrNpO_3$	orthorhombic	428	30.6
	$NpGeO_4$	tetragonal	477	9

[a] No order above 4.2 K.

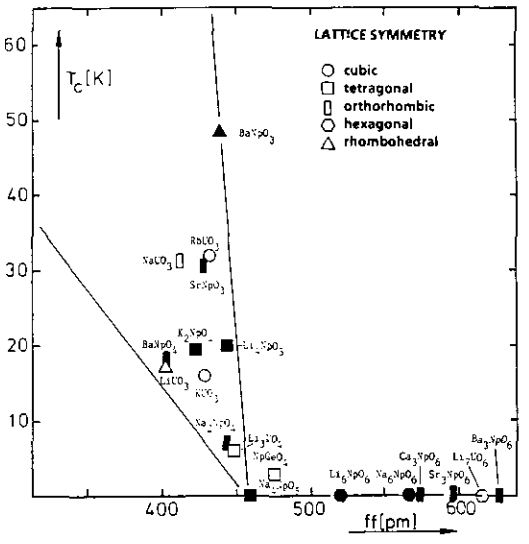

FIG. 8. Transition temperatures plotted versus the An–An distance.

tance which can be estimated from Fig. 8 by extrapolation to approximately 460 pm. Most strikingly, the existence of this critical distance is revealed by the fact that Li_4NpO_5 (ff = 443.2 pm) orders magnetically and Na_4NpO_5 (ff = 461.1 pm) with exactly the same lattice structure but different lattice constants does not (*20*).

Indeed, this is not too surprising, since the strength of the superexchange interaction strongly depends on the exchange integral, which itself depends on the degree of overlap of the orbitals involved and hence, on the distance between paramagnetic centers. Above this critical distance superexchange, i.e., magnetic ordering (above 2 K), is not possible due the smallness of the exchange interactions. Below this value, magnetic ordering should occur, if allowed by the coordination of the magnetic ion and the lattice symmetry.

The only exception to this systematics is the tetragonal $NpGeO_4$ which exhibits magnetic ordering at 8 ± 4 K, with an *An–An* distance of 476.7 pm (over oxygen ions). Its lattice contains bent *–An–O–An–* chains. Therefore, it must be concluded that the overlap of the involved orbitals is facilitated due to the angle in the *–An–O–An–* bonds. However, a systematics cannot be established due to a lack of further experimental data.

5. Conclusions

All ternary actinoid oxides with a $[Rn]5f^0$ central ion exhibit a temperature-independent, paramagnetic susceptibility. Since no $5f$ electrons are available to cause this magnetism, it is postulated that there is a degree of ligand orbital admixture into the $5f$ orbitals; i.e., a nonnegligible degree of covalency is present in the *An*–O-bonds.

This effect is also observed in the oxides containing actinoid ions with a $[Rn]5f^1$ configuration. Here a constant susceptibility is superimposed on the expected temperature dependent magnetism; i.e., the magnetic moment is composed of two parts:

—the TIP part, caused by admixture of ligand electrons into $5f$ orbitals, and

—the temperature dependent part, caused by the $5f$ electrons.

The temperature dependent moment is smaller than expected from the electronic ground state, which is probably due to participation of $5f$ electrons in bonding. This would mean that the *An*–O bond in these compounds is a two-directional effect, like that established for many transitions metal complexes. Filled ligand orbitals are bonded to empty $5f$ orbitals, and filled $5f$ orbitals to empty ligand orbitals—a synergistic effect.

The low-temperature magnetic behavior of these compounds can be explained to a large extent in terms of the lattice structures, taking into account the superexchange interaction mechanism:

—*An*–O–*An* chains are necessary to provide a superexchange path, and

—a certain maximum distance between the paramagnetic ions beyond which superexchange effects lie below the temperature range investigated. This maximum distance seems to lie near 460 pm, as deduced from the data so far available.

These findings resulted from an investigation and compilation of data for thirteen $5f^0$ and nineteen $5f^{2n+1}$ systems. Therefore, it would be extremely interesting to collect more experimental data on this class of compounds to test the established systematics more profoundly. Furthermore, calculational work would be needed to put the phenomenological and qualitative findings of this work onto a sound theoretical basis, a task which unfortunately lies beyond the authors' present capabilities. Therefore, with this work we would like to stimulate both experimentalists and theoreticians to continue the investigations and to elaborate on these relations in a more quantitative manner.

6. References

1. W. Rüdorff and W. Menzer, *Z. Anorg. Allg. Chem.* **292,** 188 (1957).
2. S. Kemmler-Sack, E. Stumpp, W. Rüdorff, and H. Erfurth, *Z. Anorg. Allg. Chem.* **354,** 287 (1967).
3. B. Kanellakopulos, unpublished results. Kernforschungszentrum Karlsruhe.
4. B. Kanellakopulos, E. Henrich, C. Keller, F. Baumgärtner, E. König, and V. P. Desai, *Chem. Phys.* **53,** 197 (1980).
5. B. Kanellakopulos, *Chem. Z.* **97,** 515 (1973).
6. B. Kanellakopulos and R. D. Fischer, *in* "Gmelins Handbuch der Anorganischen Chemie," Part A2, Transurane.
7. C. Miyake, K. Fuji, and S. Imoto, *Chem. Phys. Lett.* **61,** 124 (1979).
8. C. Miyake, H. Takeuchi, H. Ohya-Nishiguchi, and S. Imoto, *Phys. Status Solidi* **74,** 17 (1982).
9. C. Miyake, K. Fuji, and S. Imoto, *Chem. Phys. Lett.* **46,** 349 (1977).
10. J. Jové, F. Nectoux, A. Tabuteau, and M. Pagés, *in* "International Conference on the Applications of the Moessbauer Effect," *Proc. Indi. Sci. Acad. Phys. Sci.* **40,** 580 (1982).
11. F. Nectoux, J. Jové, A. Cousson, M. Pagés, and J. Gal, *J. Magn. Magn. Mater.* **24,** L113 (1981).
12. B. Kanellakopulos, C. Keller, R. Klenze,

AND A. H. STOLLENWERK, *Physica B* **102,** 221 (1980).

13. E. KÖNIG, C. RUDOWICZ, V. P. DESAI, AND B. KANELLAKOPULOS, *J. Chem. Phys.* **78,** 5764 (1983).
14. M. BICKEL, Kernforschungszentrum Karlsruhe 4109 (1986).
15. M. BICKEL, B. KANELLAKOPULOS, H. APPEL, H. HAFFNER, AND S. GEGGUS, *J. Less-Common Met.* **121,** 291 (1986).
16. S. GEGGUS, G. ADRIAN, H. APPEL, M. BICKEL, H. HAFFNER, AND B. KANELLAKOPULOS, *in* "Royal Society of Chemistry, 26th Moessbauer Discussion Group Meeting, University of East Anglia, Birmingham, 8–10 July 1985."
17. M. BICKEL, G. ADRIAN, B. KANELLAKOPULOS, H. HAFFNER, S. GEGGUS, AND H. APPEL, *Inorg. Chim. Acta* **140,** 101 (1987).
18. H. APPEL, M. BICKEL, S. MELCHIOR, B. KANELLAKOPULOS, AND C. KELLER, *J. Less-Common Met.* **162,** 323 (1990).
19. M. BICKEL AND B. KANELLAKOPULOS, *J. Less-Common Met.* **163,** L19 (1990).
20. M. BICKEL, B. KANELLAKOPULOS, AND B. POWIETZKA, *J. Less-Common Met.* **170,** 161 (1991).
21. M. BICKEL, B. KANELLAKOPULOS, AND B. POWIETZKA, *J. Alloys Compounds* (formerly *J. Less-Common Met.*) **187,** 17 (1992).
22. E. HENRICH, Dissertation, Universität Heidelberg (1971).
23. SPITSYN *et al., J. Inorg. Nucl. Chem.* **31,** 2733 (1969).
24. R. BROCHU AND J. LUCAS, *Bull. Soc. Chim.* **12,** 4764 (1967).
25. R. D. SHANNON, *Acta Crystallogr. Sect. A,* **32,** 751 (1976).
26. E. SIMONI, H. ABAZLI, A. COUSSON, AND M. PAGÉS, *Radiochem. Radioanal. Lett.* **49,** 37 (1981).
27. J. H. VAN VLECK, "The Theory of Electric and Magnetic Susceptibilities," p. 244. Oxford Univ. Press (London) 1965.
28. C. MIYAKE, M. KANAMARU, H. ANADA, S. IMOTO, AND S. KAWANO, *J. Nucl. Sci. Technol.* **22,** 653 (1985).
29. D. J. LAM AND A. T. ALDRED *in* "The Actinides: Electronic Structure and Related Properties" (A. J. Freeman and J. B. Darby Jr., eds.), p. 109, Academic Press, New York/London (1974).
30. P. G. HURAY AND S. E. NAVE, *in* "Handbook of the Physics and Chemistry of the Actinides" (A. J. Freeman and G. H. Lander, Eds.), p. 360, North–Holland, Amsterdam (1987).
31. J. C. LIVET, Thèse Université de Rennes (1978).