

# A Consideration of the Thermodynamic and Magnetic Properties of NaCl-Type Uranium, Neptunium, and Plutonium Compounds

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Received January 31, 1994; in revised form June 1, 1994; accepted July 13, 1994

Thermodynamic and magnetic properties of NaCl-type uranium, neptunium, and plutonium compounds were considered from their bonding nature. The number of electrons in a molecule participating and not participating in bonding was determined from the lattice parameter. For uranium compounds, a linear relationship was found between binding energy and bonding electron density. The paramagnetic effective moment changed with the number of electrons not participating in bonding as anticipated from the L-S coupling model based on the number of *f* electrons. © 1995 Academic Press, Inc.

## 1. INTRODUCTION

Many interesting properties of actinide elements or compounds are usually related to the complex behavior of 5*f* electrons. Depending on the circumstances surrounding the actinides, they are partly localized to the atom on one occasion or delocalized into itinerant conduction electrons on another occasion. Among the actinide compounds, several properties of NaCl-type *MX* compounds (*M*, actinide; *X*, metalloid) including monocarbide, mononpnictide, and monochalcogenide have been studied owing to the simplicity of structure and the appearance of ferromagnetic or antiferromagnetic ordering in most compounds.

About four decades ago, Rundle postulated the bonding character of carbides and nitrides of the transition metal, lanthanide, and some actinide elements (1) by analyzing the lattice parameter using the Pauling relation dealing with the bonding length and bond number (2). For uranium compounds, thereafter, Adachi gave a hint for explaining the values of ordered magnetic moments (3) in a similar manner as Rundle. At present, the experimental data for their thermodynamic and magnetic properties are fairly well accumulated although the former are limited to mainly uranium compounds. Such circumstances stimulate us to analyze the lattice param-

eters of NaCl-type compounds of uranium, neptunium, and plutonium.

In this study, the thermodynamic and magnetic properties of *MX* compounds are considered from the viewpoint of their bonding nature. Binding energy and effective magnetic moment are examined on behalf of thermodynamic and magnetic properties, respectively. At first, we calculate the number of electrons participating and not participating in bonding from the lattice parameters of the *MX* compounds, using the Pauling equation given in the following section. In Section 3, the relationship between the number of bonding electrons and the binding energy from literature values are surveyed. Speculation about the relationship between the number of electrons not participating in bonding and the effective magnetic values is also made in Section 4. The results are summarized in the last section.

## 2. METHOD OF ANALYSIS OF THE LATTICE PARAMETER

### 2.1. Pauling Equation

In the mid-1940s, Pauling proposed the following equation dealing with the bond length and bond number with regard to the bonding of metals and metallic compounds (2).

$$R = R(1) - 0.3 \log N, \quad [1]$$

where *R* is the atomic bond radius, *R*(1) is the single bond radius, namely, the bond radius for the case in which one pair of electrons participates in the bonding, and *N* is the bond number indicating the number of electrons participating in the bonding. This relation can be applied to the present *MX* compounds as

$$D(M-X) = R_M(1) + R_X(1) - 0.6 \log N, \quad [2]$$

where *D*(*M-X*) is the *M-X* atomic distance, and *R*<sub>*M*</sub>(1)

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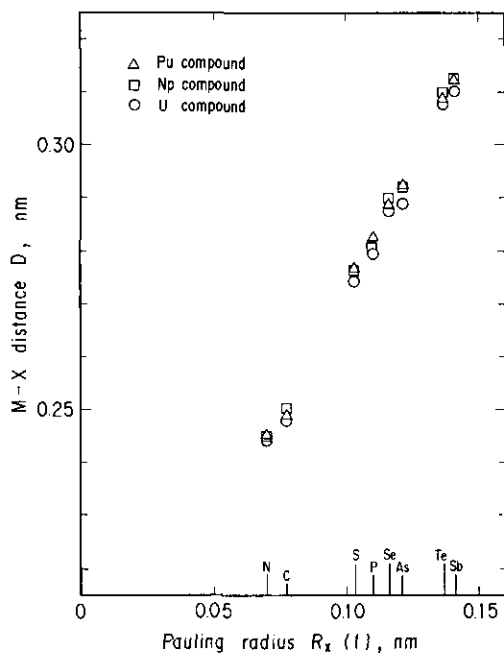


FIG. 1. Relationship between the  $M-X$  atomic distance and the single bond radius given by Pauling.

and  $R_X(1)$  are the single bond radii of actinide and metalloid, respectively.

In Eq. [2], we can easily obtain  $D(M-X)$  from the lattice parameter of  $MX$  compounds. As for metalloids, Pauling gave the covalent radius to  $R_X(1)$  (2). Figure 1 shows the relationship between  $D(M-X)$  and  $R_X(1)$  given by Pauling for  $MX$  compounds. Fairly good linearity encouraged us to use the Pauling radius as  $R_X(1)$ . For  $R_M(1)$ , Pauling gave a value of 0.1415 nm to uranium. However,  $R_M(1)$  might change with the material system considered. Hence, we arbitrarily used 0.1524 nm as the  $R_M(1)$  for uranium, which is a similar value to that which Adachi used about 25 years ago (3). Then we assumed 0.1527 and 0.1530 nm for neptunium and plutonium, respectively. The probable reason for this assessment is that the covalent character might be expected in the  $M-X$  bonding at least (1) and the covalent radius of actinides increases with the atomic number from thorium to plutonium (4). In fact, the lattice parameters tend to increase gradually in the present uranium, neptunium, and plutonium compounds in order although a few exceptions exist.

## 2.2. The Number of Bonding Electrons

From the  $M-X$  and  $M-M$  atomic distances and the single radii mentioned above, the bond number can be calculated by Eq. [2] or [1], from which the number of bonding electrons per molecule  $N_B$  is obtained as follows. In the present case, there are six  $M-X$  and  $M-M$  bonds respectively in one molecule. Since the bond number re-

TABLE 1  
The Lattice Parameter, Bond Numbers, Number of Bonding Electrons  $N_B$ , Number of Electrons Not Participating in Bonding  $N_L$ , and Total Number of Valence Electrons  $N_T$  in NaCl-type Uranium, Neptunium, and Plutonium Compounds

Compound	Lattice parameter (nm)	Bond number		$N_B$	$N_L$	$N_T$
		$M-X$	$M-M$			
UC	0.49605	0.491	0.171	7.951	0.049	8
UN	0.48887	0.429	0.208	7.651	1.349	9
UP	0.5589	0.520	0.031	6.611	2.389	9
UAs	0.5779	0.551	0.019	6.830	2.170	9
USb	0.62091	0.520	0.006	6.306	2.694	9
US	0.5484	0.486	0.041	6.329	3.671	10
USe	0.5750	0.480	0.020	6.007	3.993	10
UTe	0.6163	0.487	0.007	5.922	4.078	10
NpC <sup>a</sup>	0.49949	0.465	0.160	7.499	1.321	8.82
NpN	0.48987	0.426	0.207	7.601	2.399	10
NpP	0.56148	0.500	0.030	6.361	2.638	10
NpAs	0.58389	0.496	0.016	6.152	3.848	10
NpSb	0.62485	0.487	0.005	5.913	4.087	10
NpS	0.5532	0.448	0.037	5.827	5.173	11
NpSe	0.5804	0.438	0.018	5.472	5.528	11
NpTe	0.6198	0.461	0.006	5.601	5.399	11
PuC <sup>b</sup>	0.4968	0.495	0.176	8.056	1.624	9.68
PuN	0.4905	0.426	0.209	7.613	3.387	11
PuP	0.5663	0.461	0.027	5.858	5.142	11
PuAs	0.58610	0.481	0.016	5.964	5.036	11
PuSb	0.62397	0.502	0.006	6.086	4.914	11
PuS	0.55400	0.447	0.037	5.807	6.193	12
PuSe	0.577	0.473	0.020	5.917	6.083	12
PuTe	0.6183	0.480	0.007	5.833	6.167	12

<sup>a</sup> Atomic C/Np ratio is 0.91.

<sup>b</sup> Atomic C/Pu ratio is 0.84.

fers to the number of shared electron pairs,  $N_B$  could be calculated by multiplying 12 by the total  $M-X$  and  $M-M$  bond numbers. In this procedure, the contribution from the  $X-X$  and other second nearest neighbor bonds was small enough to be neglected.

Table 1 summarizes the obtained  $M-X$  and  $M-M$  bond numbers and  $N_B$  as well as the lattice parameters of the compounds concerned in this study. Most of the lattice parameters were quoted from the paper reviewed by Benedict (5). It is seen from the table that the  $M-X$  bond number is approximately 0.5 and the  $M-M$  bond number is less than 0.05 except in the case of carbides and nitrides. The value of 0.5 indicates that one electron participates in bonding, which could be understood by the concept of half-bond introduced by Rundle (1). The number of bonding electrons of carbides and nitrides is found to be larger than that of the other compounds due to the contribution of  $M-M$  bonding.

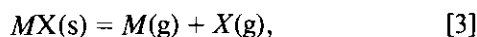
### 2.3. The Number of Electrons Not Participating in Bonding

The number of electrons not participating in bonding  $N_L$  could be obtained by subtracting the number of bonding electrons from the total number of valence electrons in a molecule  $N_T$ . The electronic configuration of uranium, neptunium, and plutonium atoms with their ground state out of the closed shell is written as  $5f^36d7s^2$ ,  $5f^46d7s^2$ , and  $5f^67s^2$ ; the number of electrons outside the Rn core is 6, 7, and 8, respectively. On the other hand, the present metalloid of group  $N$  has the electronic configuration of  $s^2p^{N-2}$  out of the respective closed shell. Here, we assume that the electrons in the metalloid capable of participating in bonding are only  $p$ -state ones, because the contribution of  $p$ -state electrons seems to predominate in an octahedral configuration of the presently studied  $MX$  compounds.

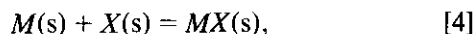
Considering the total number of valence electrons  $N_T$  as a sum of electrons outside the Rn core from actinide and  $p$ -state electrons from metalloid,  $N_T$  and the number of electrons not participating in bonding  $N_L$  in  $MX$  compounds obtained are also given in Table 1. In this table, simple corrections are made for  $N_T$  in neptunium and plutonium carbides which always have a hypostoichiometric composition; i.e., the number of  $p$ -state electrons in carbon is calculated by multiplying 2 by the reported atomic C/Np or C/Pu ratio.

### 3. THERMODYNAMIC CONSIDERATION: BINDING ENERGY AND BONDING ELECTRON DENSITY

Among thermodynamic properties, binding energy is dealt with in this section since it might be related to the number of bonding electrons. Here, we define the binding energy of  $MX$  compounds as the enthalpy change of the following reaction, i.e., the atomization energy at 298 K,



where the symbols g and s in parentheses stand for gaseous and solid states, respectively. For most uranium compounds, the enthalpy change of the reaction,



is given as a standard enthalpy of formation. In case of nitrides,  $X(s)$  in Eq. [4] is substituted by  $1/2N_2(g)$ . For neptunium and plutonium compounds, only the thermodynamic data of carbide or nitride are available. To obtain the binding energy, i.e., the enthalpy change of Eq. [3], it is necessary to consider the sublimation enthalpy of actinide and metalloid represented by the reactions



TABLE 2  
Literature Values Used for Calculation of the Binding Energy

Reaction	$\Delta H_{298}^\circ$ (kJ/mole)	References
U(s) + C(s) → UC(s)	-97.9	(6)
U(s) + $\frac{1}{2}N_2(g)$ → UN(s)	-290.8	(6)
U(s) + P(s) → UP(s)	-268	(6)
U(s) + As(s) → UAs(s)	-234	(6)
U(s) + Sb(s) → USb(s)	-138	(6)
U(s) + S(s) → US(s)	-322	(6)
U(s) + Se(s) → USe(s)	-276	(6)
U(s) + Te(s) → UTe(s)	-182	(6)
Np(s) + 0.91C(s) → NpC <sub>0.91</sub> (s)	-71	(6)
Pu(s) + $\frac{1}{2}N_2(g)$ → PuN(s)	-299	(6)
Pu(s) + 0.84C(s) → PuC <sub>0.84</sub> (s)	-45.2	(6)
C(s) → C(g)	717	(7)
$\frac{1}{2}N_2(g)$ → N(g)	473	(7)
P(s) → P(g)	316	(9)
As(s) → As(g)	302	(8)
Sb(s) → Sb(g)	262	(7)
S(s) → S(g)	277	(9)
Se(s) → Se(g)	235	(8)
Te(s) → Te(g)	196	(7)
U(s) → U(g)	536	(6)
Np(s) → Np(g)	465	(6)
Pu(s) → Pu(g)	342	(6)

$$X(s) = X(g), \quad [6]$$

In calculating the binding energy, the enthalpy changes of Eqs. [4] and [5] were quoted from the table summarized by Morss (6) and those of Eq. [6] were from other literature (7-9). In Table 2, the numerical values used in the calculation are given. Figure 2 shows the relationship between the binding energy and the number of bonding electrons per unit bond length which we here named bonding electron density. The bonding electron density in this case means a sum of  $N_B(M-X)/D(M-X)$  and  $N_B(M-M)/D(M-M)$  and the errors in it caused by the uncertainties in the lattice parameters are also shown in the figure where we assume that the lattice parameters listed in Table 1 contain a marginal error in the last significant figure; in Fig. 2 they are indicated by error bars. With regard to the uranium compounds, an almost linear relationship is seen in the figure where the solid line was drawn by a least-squares method. This suggests that the binding energy of the compounds could be estimated from the bonding electron density which is easily calculated from the lattice parameter. Furthermore, the appropriate Pauling radius for uranium we assumed in Section 2.1 is suggested from the linearity.

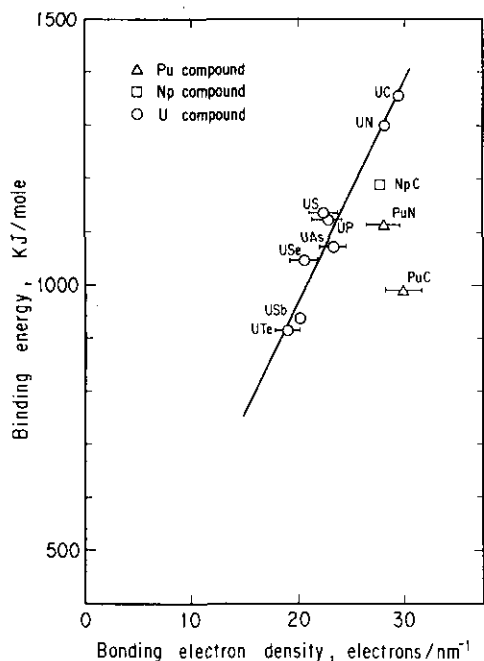


FIG. 2. Relationship between the binding energy and the bonding electron density in  $MX$  compounds.

On the other hand, data points are too few to discuss the results for neptunium and plutonium compounds. However, the following speculation could be made for the relation with the results for uranium compounds. Brewer suggested that the sublimation of lanthanide metal is accompanied by the change in valency with the change in electronic configuration and hence the correction of sublimation enthalpy by promotion energy is necessary to know the true binding energy (10). The same will be applicable for actinides. Imoto discussed the cohesive energy with the valency of actinide metals and proposed that the light actinide metals from thorium to plutonium have a tetravalent ion core because the corrected cohesive energies calculated from promotion energies to  $5f^{N-4}6d^{27}s^2$  conform to atomic volume behavior (11). In such circumstances the promotion energies to be added to Eq. [5] increase in uranium, neptunium, and plutonium compounds in order (4). Indeed, the data points for neptunium and plutonium compounds in Fig. 2 come close to the line for uranium compounds if this correction is made to Eq. [5]. In all events, still more measurements of thermodynamic properties are expected.

#### 4. MAGNETIC CONSIDERATION—EFFECTIVE MAGNETIC MOMENT AND THE NUMBER OF LOCALIZED ELECTRONS

The number of electrons not participating in bonding  $N_L$  is given in Section 2.3. In this section we assumed them

to be localized  $M$  atoms and designate them "localized electrons" in order to discuss a correlation with the magnetic properties of  $MX$  compounds. Compared with thermodynamic properties, there exist many experimental results of magnetic properties for the present compounds. Among some magnetic values the paramagnetic effective moment  $\mu_{\text{eff}}$  is most characterized. Figure 3 shows the relationship between the reported paramagnetic effective moment  $\mu_{\text{eff}}$  and the number of localized electrons. Most of the experimental data are quoted from the table in Fournier and Troc's text (12). In general, the effective magnetic moment tends to increase as the number of localized electrons increases from 0 to 3; then it tends to decrease as their number increases to 6. On the other hand, the solid line in the figure represents the results calculated from the L-S coupling model as a function of the number of  $f$ -electrons. Except for the cases of neptunium nitride, plutonium carbide, and nitride, the data points are almost on the solid line. This could be proof of the assumption that the electrons not participating in bonding are localized to  $M$  atoms. Furthermore, Fig. 3 gives us a hint about the valency of actinide in  $MX$  compounds. It is seen that the points for plutonium monochalcogenides cluster around 6 localized electrons, plutonium mononitrides and neptunium monochalcogenides around 5, and neptunium mononitrides and uranium monochalcogenides around 4. For uranium mononitrides, the number of localized electrons is situated between 2 and 3. From these findings it is suggested that uranium, neptunium, and plutonium in their monochalcogenides are divalent and neptunium and plutonium in their mononitrides ex-

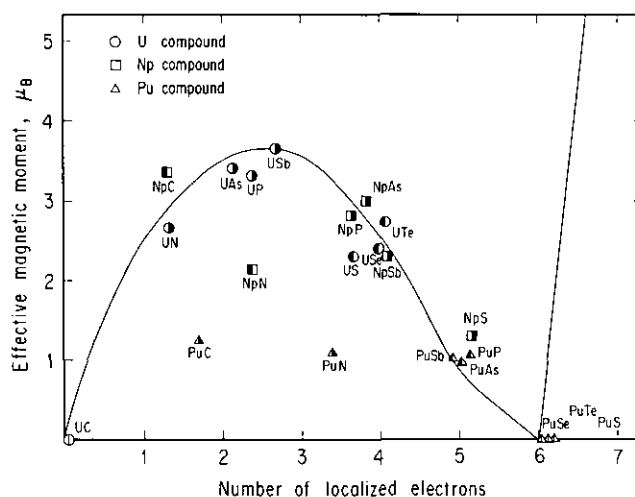


FIG. 3. Relationship between the paramagnetic effective moment and the number of localized electrons in  $MX$  compounds. The symbols  $\odot$ ,  $\blacksquare$ , and  $\blacktriangle$  denote ferromagnetism, while  $\circ$ ,  $\square$ , and  $\triangle$  denote antiferromagnetism. The symbols  $\circ$ ,  $\square$ , and  $\triangle$  denote temperature-independent paramagnetism.

cept nitrides are trivalent. For uranium in mononitrides the valency would be almost 3. On the other hand, some different characteristics are seen in carbides and nitrides, although the reason is not clear at the moment. It may well be that the concept of hybridized orbital is adopted in the bonding of such metalloids.

A relationship between magnetic order and the number of localized electrons is also found. Most of the uranium and plutonium compounds having more than 3 localized electrons represent ferromagnetism and those less than 3 represent antiferromagnetism. In contrast, the opposite tendency is seen for neptunium compounds. An exceptional compound is plutonium nitride representing antiferromagnetism. Uranium carbide with almost no localized electrons and plutonium monochalcogenides having about 6 localized electrons represent temperature-independent paramagnetism.

## 5. SUMMARY

In this study, the number of electrons participating and not participating in bonding in NaCl-type uranium, neptunium, and plutonium compounds was determined from their lattice parameters. For uranium compounds, a linear relationship was found between binding energy and bonding electron density. The gap existing among the compounds was interpreted by the difference in the promotion energy of actinides. Paramagnetic effective moment of the compounds changed with the number of electrons not participating in bonding as anticipated from the L-S coupling model, from which the information about the valency of actinide was obtained. It was inferred from the present results that carbide and nitride have peculiar bonding characteristics among *MX* compounds.

The analytical method employed in this study is somewhat traditional compared with a modern theoretical calculation. In this sense, the results induced from this study are a proposal for arranging complex properties of NaCl-type actinide compounds. In general, however, actinide compounds are not easy to deal with and the elements

themselves are precious. So this kind of study will be useful for understanding the basic properties relating to the bonding of the compounds, especially those after americium in the periodic table with which one encounters experimental difficulties. The number of *5f* electrons will increase with atomic number and be even more localized in such elements. While no thermodynamic data are available at the moment, a few magnetic data of americium and curium compounds exist (12). A qualitative survey revealed that the number of localized electrons in americium mononitrides representing paramagnetism is around 6 and that in monochalcogenides showing a rapid increase in  $\mu_{\text{eff}}$  approaches 7.

## ACKNOWLEDGMENTS

The authors thank Drs. E. Tachikawa and M. Handa for their interest in this study. Thanks are also given to Prof. Dr. S. Imoto of the Fukui Institute of Technology for valuable comments.

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