

## Magnetic Susceptibility of the Uranium Nitrides

ROBERT TROĆ

*Institute for Low Temperature and Structure Research, Polish Academy of Sciences  
Wrocław, Poland*

Received February 12, 1974

The magnetic susceptibility of UN, and of the higher uranium nitrides has been measured over a wide temperature range, i.e., 4.2–950 K. A large temperature-independent term  $\chi_0$  equal to  $310 \pm 10 \times 10^{-6}$  emu/mole has been derived from the total susceptibility data of UN. The obtained  $\chi_M$  values of UN are also related to the Knight shift data from literature. For the higher nitrides  $U_2N_{3+x}$  the magnetic susceptibility has been measured for N:U ratios between 1.55 and 1.80. Antiferromagnetic phase transitions have been found for all the examined compositions. The transition temperature  $T_N$  gradually decreases as the nitrogen content increases, varying from 94 K for  $UN_{1.55}$  to about 8 K for the maximum composition of  $UN_{1.80 \pm 0.02}$ . The magnetic properties of the higher nitrides are discussed in terms of mixed valency states, either  $U^{4+}$  and  $U^{6+}$  or  $U^{4+}$  and  $U^{5+}$  for the stoichiometric  $U_2N_3$ .

### 1. Introduction

Though up to now the uranium nitrides have been the subject of quite intensive studies, there still remain many unresolved problems. On the basis of numerous investigations reported in the literature, the following nitride phases in the U–N system are certain to exist: the uranium mononitride UN, the cubic (bcc) and hexagonal (hcp) sesquinitrides, and a nitrogen deficient  $UN_{2-x}$  phase.

Being a very stable compound, UN crystallizes in the rock-salt structure and shows a very narrow range of existence. In contrast, the cubic sesquinitride exists within a wide composition range with nitrogen excess,  $U_2N_{3+x}$ . This broad-composition compound has the  $Mn_2O_3$  type structure (in rare earth oxides, Type C) and exhibits substoichiometry, with the N:U ratio well above 1.5 for the lower, and about 1.75 for the upper limit. The U-rich phase limit was determined by several authors who studied the pressure-composition isotherms for  $U_2N_{3+x}$ . On one hand Bugl and Bauer (1), and Tagawa (2) have established this boundary to be  $UN_{1.54}$ , on the other Lapat and Holden (3), and Müller and Rogoss (4) have reported this

boundary to be  $UN_{1.57-1.59}$ ; all values are given at about 800°C. The hexagonal  $U_2N_3$  has the  $La_2O_3$  type structure (in rare earth oxides, Type A). Its detailed magnetic properties will be given elsewhere.

Only a little is known about the  $UN_{2-x}$  phase. Previously, the  $CaF_2$  type structure (fcc) was assigned to this phase (5, 6) because of the lack in the X-ray diffraction patterns of the weak substructural reflections characteristic of the  $Mn_2O_3$  phase. More recently, the cubic primitive  $\gamma$ -phase with a composition of  $UN_{1.90 \pm 0.02}$  has been obtained by the high-temperature ammonolysis of  $UF_4$  in a stream of  $NH_3$  at 900°C (7). In contrast to the highest available nitride phases, obtained in the reaction of nitriding uranium and being usually highly distorted, the  $\gamma$ - $UN_{1.90}$  phase shows very sharp X-ray patterns. Due to the appearance of weak reflections also in this case, requiring a doubling of the lattice unit, Berthold et al. (7) have pointed out that the same crystal structure should also have phases of the  $UN_{2-x}$  type.

Magnetic measurements on UN were first carried out over a relatively narrow range of temperatures, e.g., between 80 and 300 K

by Trzebiatowski et al. (8) and by Allbut et al. (9). Recently, susceptibility measurements on UN in a wide temperature range from 4.2 to 1000 K have been done by Raphael and de Novion (10), and by Ohmichi et al. (11). Since there is an appreciable discrepancy in the results obtained by these two groups of authors, new susceptibility measurements on the uranium mononitride, performed also over a wide range of temperatures, will be presented here.

So far the only paper (6) on the magnetic properties of the higher uranium nitrides is limited to the temperature region 80–300 K. Therefore, in the present work the magnetic measurements are extended both to lower and higher temperatures.

## 2. Experimental

Uranium nitrides were prepared by various methods depending on the composition. The nitrides with the composition between  $UN_{1.5}$  and  $UN_{1.72}$  were obtained by treating fine-grained uranium powder with pure nitrogen, obtained from a thermal decomposition of sodium azide, as described earlier (6). The nitriding process was being performed at temperatures between 600 and 800°C under a nitrogen pressure less than 1 atm. The resulting nitrides were next placed in evacuated quartz ampoules and additionally homogenized at temperatures from 800 to 1000°C depending on the composition, during several days. To obtain pure  $UN_{1.55}$  without any traces of the hcp sesquinitride, which is a ferromagnet, it was necessary to hold the sample at a temperature of 800°C for two weeks. For the nitrides containing more nitrogen the homogenization could be performed at higher temperatures without forming the hcp phase.

The higher nitrogen-content phase  $UN_x$ ,  $1.75 \leq x \leq 1.81$ , was obtained by passing well-purified nitrogen or gaseous ammonia on uranium hydride at temperatures ranging from 400 to 600°C. The nitride with the highest available U:N ratio equal to  $1.80 \pm 0.02$  was obtained in the ammonia process at 400°C lasting for 24 hr. The product of this

reaction was a very fine powder, being strongly unstable in air. Hence, all operations were carefully carried out under argon atmosphere. Attempts to homogenize these highest nitrides failed because of the appearance of high nitrogen pressure on heating. In turn the uranium mononitride was obtained by the thermal decomposition of the nitrides with larger nitrogen content in high vacuum at 1400°C for 2–3 hr.

The composition of the nitrides was determined either by measuring the volume of the absorbed nitrogen or by checking the weight before and after nitrification, employing special conditions. Additionally, the uranium content in the samples was determined gravimetrically by oxidizing the nitrides to  $U_3O_8$ , on heating the samples in air at a temperature of 900°C for 4 hr.

All nitride samples were analysed by X-ray investigations. Except for UN, only the nitrides with intermediate compositions showed fairly sharp X-ray patterns, whereas the samples with the highest nitrogen content gave very diffused reflections, particularly in the higher-angle region. The lattice constants were determined using a 114 mm diam powder camera and tungsten as reference.

Magnetic measurements were performed over the temperature region 4.2–1000 K by the Faraday method at several magnetic field strengths, using at lower temperatures an RH-Cahn Electrobalance as described elsewhere (12). No ferromagnetic contamination, above all of the hcp nitride was detected in the samples.

## 3. Results

### 3.1. Uranium Mononitride

The results of the magnetic measurements on UN are presented in Fig. 1. The susceptibility maximum appears at  $T_N = 53 \pm 1$  K, in agreement with earlier works (10, 11, 13). As is seen from Fig. 1, the magnetic susceptibility of UN obeys the Curie-Weiss law up to 450 K, yielding  $\theta = -250 \pm 10$  K and  $\mu_{\text{eff}} = 2.93 \mu_B$ . Exactly the same magnetic parameters were obtained by Ohmichi et al. (11) in a little wider temperature range, up to 600 K.

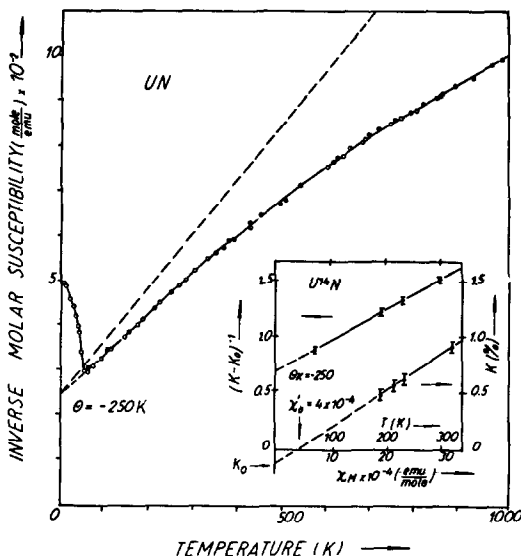


FIG. 1. Inverse susceptibility of UN as a function of temperature. The inset is the Knight shift from Ref. (15) vs molar susceptibility, as well as  $(K-K_0)^{-1}$  as a function of temperature for  $U^{14}N$ . The dashed line is the  $\chi^{-1}$  vs  $T$  function upon subtracting the temperature-independent term.  $\circ$  Sample 1;  $\bullet$  Sample 2.

Noticeably different characteristics have been given by Raphael and de Novion (10) between 100 and 300 K, namely  $\theta = -270$  K and  $\mu_{\text{eff}} = 2.80 \mu_B$ , and the value of the magnetic susceptibility is lower by about 10% at room temperature. Such a difference has been explained later by de Novion and Costa (14) as being caused by the presence of 2000 ppm of carbon in the UN sample used in earlier experiments.

Similar to the investigations of Refs. (10) and (11), the susceptibility of UN deviates markedly from the Curie-Weiss behavior at higher temperatures. However, in the highest temperature region the agreement is not so good as at lower temperatures, between the present susceptibility data and those in Ref. (11). The present values are  $\theta = -700$  K and  $\mu_{\text{eff}} = 3.6 \mu_B$  in the interval 750–1000 K, which are to be compared to  $-380$  K and  $3.2 \mu_B$ , respectively.

It is known that the deviation from the straight line of the  $\chi^{-1}$  vs  $T$  function is due to the contribution of the temperature-independent term  $\chi_0$  arising mainly from the Pauli and Van Vleck paramagnetism. This

in general, can be determined by fitting the obtained susceptibility results to the formula:  $\chi = \chi_0 + C/(T - \theta)$ . A straight-line dependence (dashed line in Fig. 1) is obtained by assuming  $\chi_0$  to be  $310 \pm 10 \times 10^{-6}$  emu/mole for the whole temperature range studied. Upon separating  $\chi_0$  from the measured susceptibility, the magnetic characteristics are:  $\theta = -200$  K and  $p = 2.5 \mu_B$  ( $p$  is the paramagnetic moment assumed to be directly attributable to the ground state of the magnetic ion). The same parameters given in Ref. (10) are:  $500 \times 10^{-6}$  emu/mole,  $-160$  K and  $2.06 \mu_B$ , respectively.

The  $\chi_M$  data of UN determined at present have been related to the Knight shift of  $U^{14}N$  given by Kuznietz (15). In this way one obtains a straight line for the  $K$  vs  $\chi_M$  function, as illustrated in the inset in Fig. 1. New values of  $K_0$  and  $\chi_0'$  (defined in Fig. 1) amounting to  $-15 \times 10^{-4}$  and  $400 \times 10^{-6}$  emu/mole, respectively, are obtained instead of the corresponding values of  $-31.5 \pm 3.5 \times 10^{-4}$  and  $760 \times 10^{-6}$  reported by Kuznietz (15) who took the  $\chi_M$  values from earlier works (8, 9). This difference is further reflected in the change of the slope of the  $K$  vs  $\chi_M$  function, from  $4.2 \pm 0.25$  mole/emu to  $3.4$  mole/emu (about 20%) after employing the present  $\chi_M$  data. Such a change in the term  $\alpha$  affects of course the values of the exchange constants derived by Kuznietz (15). Furthermore, the plot of  $(K - K_0)^{-1}$  vs  $T$  ( $K_0 = -15 \times 10^{-4}$ ), also shown in the inset in Fig. 1, yields  $\theta_K = -250$  K, in excellent agreement with the susceptibility data. Hence, it is concluded that the new susceptibility results are more consistent with the Knight shift data. The difference in the temperature-independent term  $\chi_0$  and  $\chi_0'$  is the resulting effect of at least two contributions which presently cannot be distinguished from each other: the Pauli and the Van Vleck paramagnetism.

### 3.2. The Higher Uranium Nitrides

*Lattice constants.* The lattice parameters for all the investigated higher nitrides are presented in Fig. 2 as a function of composition. For the nitrides with N:U ratio  $< 1.75$  the lattice constants lie within a range (hatched stripe in Fig. 2) limited by earlier detailed

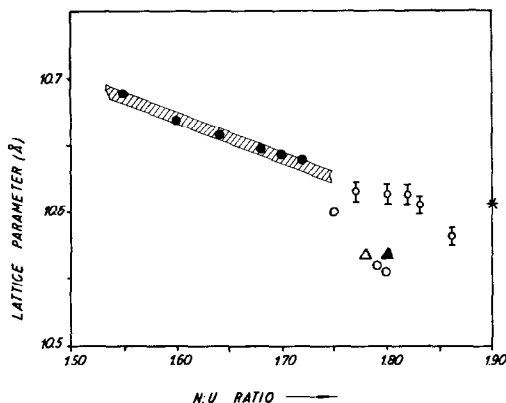


FIG. 2. Lattice constants of the higher nitrides  $U_2N_{3+x}$  as a function of the U:N ratio. The open and closed circles are the results of the present work. Open and closed triangle represents data from Refs. (19) and (18), respectively. Small open circles show the results of Ref. (7). An asterisk represents the lattice constant of  $\gamma$ - $UN_{1.9}$  from Ref. (7). The hatched stripe is explained in the text.

investigations of several authors (6, 16, 17). The region of composition with  $N:U \geq 1.75$  is still uncertain. In Fig. 2 there is distinctly seen a discontinuity in the lattice spacing in the vicinity of  $UN_{1.75 \pm 0.01}$ . The lowest value of  $a_0$  is obtained for  $UN_{1.80 \pm 0.02}$  which is equal to  $10.550 \pm 0.005$  Å. This value is rather close to the data obtained by Price and Warren (18) for  $UN_{1.80}$  ( $a_0 = 10.568 \pm 0.002$ ) and by Anselin (19) for  $UN_{1.78}$  ( $a_0 = 10.568 \pm 0.005$  Å). The X-ray photographs for samples with the composition above  $UN_{1.72}$  give strongly diffused reflections, particularly in the higher-angle region. Such a broadening causes the weak reflections to disappear and, due to this fact, the crystal structure of the  $UN_{2-x}$  phase was in earlier investigations identified as if  $CaF_2$  type.

More recently, Berthold et al. (7) have examined the reaction of UN or higher nitrides with  $N_2$  or  $NH_3$  at pressures up to 200 atm and temperatures between 400 and 600°C. They have found that this reaction leads to the maximum composition  $UN_{1.86}$  ( $NH_3$ ). The lattice parameters of their nitrides are shown in Fig. 2 by means of small circles. In general, these lattice constants are in disagreement with the present results and also with those from Refs. (18) and (19).

Furthermore, these authors have obtained the stable  $\gamma$ - $UN_{1.90 \pm 0.02}$  phase in the ammonolysis reaction, with an ordered cubic primitive structure with  $a_0 = 10.605 \pm 0.001$  Å. This value is markedly higher than that obtained for  $UN_{1.80}$  in the present work. A similar discrepancy between the lattice constants of the nitrides obtained under high pressure and the  $\gamma$ -phase has been explained by Berthold et al. (7) who pointed out that the lattice constants of the highest nitrides depend upon the degree of ordering of the crystal structure which, in turn, depends on the mechanism by which the nitrides are formed. A detailed analysis of the X-ray patterns made by Berthold et al. (7) for the  $UN_{2-x}$  phase obtained under pressure allowed them to find some additional very weak reflections besides those belonging to the pseudo fcc structure, which required them to double the unit cell.

**Magnetic measurements.** The results of magnetic measurements on higher nitrides are presented in Figs. 3-6 as well as in Table I. Figure 3 shows on an enlarged scale, the temperature variation of the inverse susceptibility in the temperature range 4.2-300 K

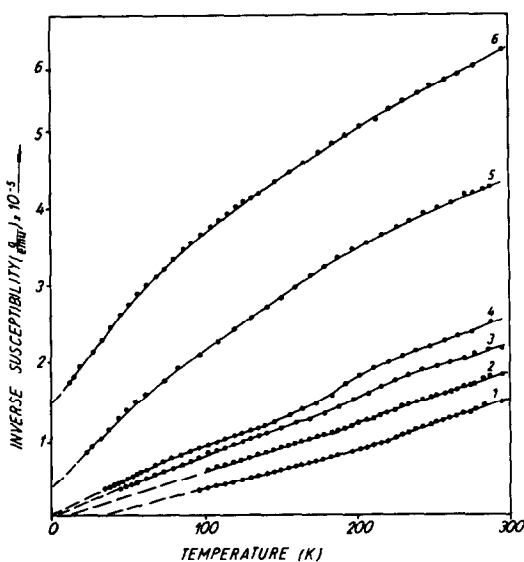


FIG. 3. Inverse susceptibility of  $U_2N_{3+x}$  as a function of temperature, in the lower temperature range up to 300 K. 1.  $UN_{1.55}$ ; 2.  $UN_{1.60}$ ; 3.  $UN_{1.64}$ ; 4.  $UN_{1.68}$ ; 5.  $UN_{1.75}$ ; 6.  $UN_{1.80}$ .

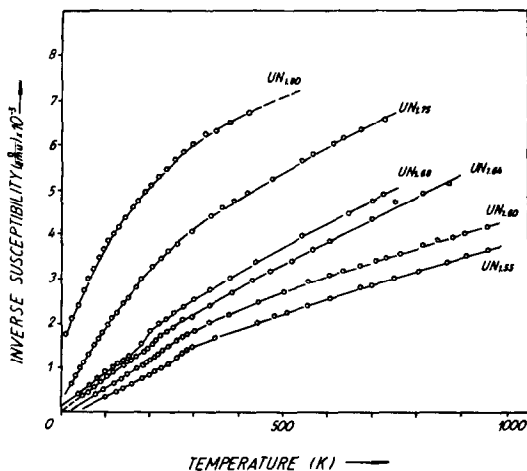


FIG. 4. Inverse susceptibility of  $U_2N_{3+x}$  as a function of temperature over the temperature range up to 950 K.

for the nitrides whose compositions are listed in Table I. It follows from Fig. 3 that there is some difference in the behaviour of the  $\chi^{-1}$  vs  $T$  curves between the nitrides  $UN_{1.55-1.68}$  and  $UN_{1.75-1.80}$ . For the former compositions one observes the inflexion of the  $\chi^{-1}$  vs  $T$  function at about 240 K for

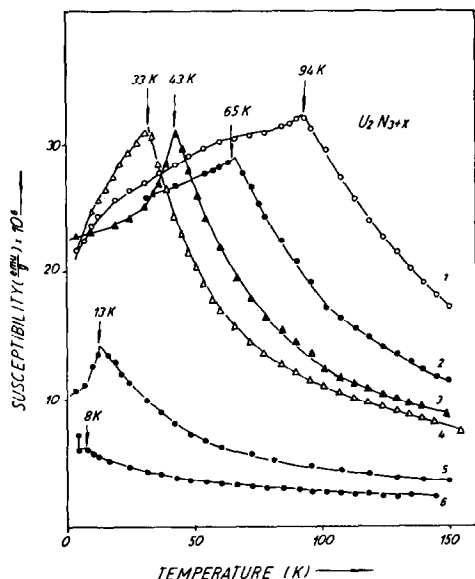


FIG. 5. Susceptibility of  $U_2N_{3+x}$  as a function of temperature at lower temperatures. Numbers 1-6 represent the compositions given in Fig. 3.

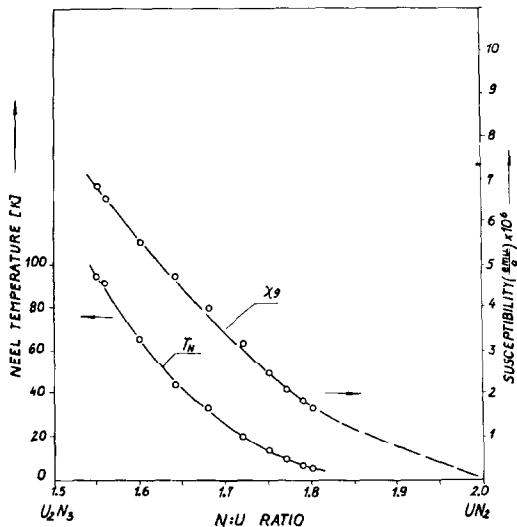


FIG. 6. Susceptibility at room temperature and Néel temperature of  $U_2N_{3+x}$  as a function of the N:U ratio.

$UN_{1.55}$ , which then moves toward lower temperatures as the nitrogen content increases. The effective magnetic moment calculated at temperatures below the inflexion for  $UN_{1.55}$  approaches the value of  $2.05 \mu_B$ , which is in fair agreement with the earlier estimation (6). On the other hand, the  $\chi^{-1}$  vs  $T$  curves for the nitrides  $UN_{1.75-1.80}$  are strongly curvilinear. Figure 4 shows the results of susceptibility from 4.2 to 950 K. It is obvious that this temperature interval is gradually being diminished from above for the highest nitrides due to their increasing tendency toward instability. It appears from Fig. 4 that the slope of the  $\chi^{-1}$  vs  $T$  functions at higher temperatures gradually increases as nitrogen content in the samples is rising.

The temperature variation of the susceptibility at lower temperatures for all the nitrides under consideration is shown in Fig. 5. As we see, the susceptibility goes through a maximum for all investigated nitrides, indicating an antiferromagnetic ordering. In the previous work (6) the susceptibility maximum at 96 K has been found only for  $UN_{1.5}$ , because of the fact that the measurements were performed in a limited temperature region, i.e., between 83 and 300 K. Now it is clearly seen that the magnetic ordering exists

TABLE I  
THE LATTICE PARAMETERS AND MAGNETIC CHARACTERISTICS OF THE URANIUM NITRIDES

Composition UN <sub>x</sub> (±0.01)	Lattice constants (±0.002 Å)	$\chi_g^{290\text{K}} \times 10^6$	$T_N$ (°K)	$\theta$ (°K)	$\mu_{\text{eff}}$ ( $\mu_B$ )
1.55	10.690	6.80	94	35	2.05
1.60	10.670	5.51	65	10	1.84
1.64	10.658	4.69	43	3	1.63
1.68	10.648	4.00	33	0	1.46
1.72	10.640	3.20	19	-5	1.23
1.75	10.600 <sup>a</sup>	2.45	13	-15	1.12
1.80 <sup>b</sup>	10.550 <sup>a</sup>	1.65	8	-65	0.91

<sup>a</sup> (±0.005 Å); <sup>b</sup> (±0.02).

not only for the U<sub>2</sub>N<sub>3+x</sub> but also for the UN<sub>2-x</sub> phase, although the highest available nitride UN<sub>1.80</sub> shows a very weakly marked maximum of the susceptibility at 8 K and a sharp increase of  $\chi$  at about 5 K. The characteristic feature of UN<sub>1.55</sub> is a convex susceptibility vs temperature curve below  $T_N$ . The Néel points and the magnetic susceptibilities at 290 K for higher uranium nitrides are shown in Fig. 6. As Fig. 6 illustrates, the susceptibility and the Néel points follow concave curves. The values of the effective magnetic moments, which are compiled in Table I, have been calculated from the straight line parts of the  $\chi^{-1}$  vs  $T$  dependences at the lowest temperatures.

The occurrence of magnetic ordering in the higher nitrides confirms the specific heat measurements performed by Counsell et al. (20). They have found  $C_p$  anomalies at 94 and 33 K for UN<sub>1.59</sub> and UN<sub>1.73</sub>, respectively, corresponding to magnetic ordering phenomena. However, the entropies of the magnetic transitions are very small and amount to 0.12 and 0.05 cal deg<sup>-1</sup> mole<sup>-1</sup>, respectively.

## 4. Discussion

### 4.1. Uranium Mononitride

The magnetic properties of UN have been intensively discussed in the literature (11, 14, 21-23). This discussion is mainly based on the assumption of either the localization of  $5f^2$

or  $5f^3$  electronic states, or in terms of an itinerant band model implying a hybridization of the  $d$ - $f$  electrons.

Uranium mononitride possesses a special intermediate position in the uranium mononitride series. It exhibits the lowest U-U spacing (3.24 Å), as well as the lowest Néel temperature (53 K) and ordered magnetic moment (0.75  $\mu_B$ ) in comparison to the remaining UV-type monocompounds. The latter compounds are believed to have a  $5f^3$  configuration (12) and can be described as U<sup>3+</sup>V<sup>2-</sup>, whereas the  $5f^2$  configuration is more applicable for uranium in UN (U<sup>4+</sup>N<sup>3-</sup>). This scheme explains a good conductivity exhibited by all these uranium-V group compounds. A change of an anion valency from -3 to -2 has been suggested, for example, in the praseodymium mononitrides by means of neutron inelastic spectroscopy when passing from PrN (24) to the other PrV compounds (25).

As a result of the change of the electronic configuration in UN the crystal-field scheme for this compound is quite different from that in the other mononitrides with octahedral symmetry. Hence, for UN a singlet ground state  $\Gamma_1$  with a next-lying triplet  $\Gamma_4$  is expected. Such a simple scheme of the crystal-field levels together with the molecular field interactions have been applied to UN by de Novion (26) to account for both the small value of the magnetic entropy and the spin-disorder resistivity. However, better agree-

ment may be achieved by taking into account a  $J$ -mixing effect in the ground state.

It should be emphasized that for UN there is a rather large contribution of the temperature-independent term  $\chi_0$  to the total susceptibility, being for example about 10 times larger than that in the case of UP and UAs (12). This probably arises from the dominant character of the Pauli paramagnetism in  $\chi_0$  as a result of the high-density state of the conduction band at the Fermi level, which has been estimated from the electronic specific-heat investigation to be 10.6 states/eV atom for UN (14), in comparison to the value of 4.1 states/eV atom for UP (27). Unfortunately, there is no successful theory which would be able to interpret uniquely the magnetic properties of the actinide compounds, having to some extent an itinerant character of the  $5f$  electrons (a very narrow  $5f$  band) which, in addition, is strongly influenced by the crystalline field.

#### 4.2. Higher Uranium Nitrides

*Symmetry considerations.* In the cubic  $Mn_2O_3$  type unit cell (space group  $Ia\bar{3}-T_h^7$ ) there are 32 uranium atoms and 48 nitrogens. The uranium atoms occupy different positions  $8b$  and  $24d$  in the unit cell, denoted U(I) and U(II), respectively. Eight U(I) are exactly fixed on the ideal fcc sites with threefold inversion symmetry ( $C_{3i}-S_6$ ), whereas 24 U(II) are located in the sites with twofold symmetry,  $C_2$  having one adjustable position,  $u = -0.015/0.018$  (28, 29). The nitrogen atoms, denoted here as N(I), are in the positions  $48e$  with  $x$ ,  $y$ , and  $z$  adjustable parameters. The nitrogen coordination around two uranium sites is shown in Fig. 7. For the  $C_2$  sites, the nitrogen atoms are situated at the corners of a very distorted cube from which two nitrogen atoms have been removed from a face diagonal, and the U(II) atoms are slightly displaced from the centre of this cube in the  $[100]$  direction. U(II) coordinates 2N(I) at the distance of 2.25 Å and 4 N(I) at about 2.33 Å. For the  $C_{3i}$  sites the missing nitrogens are from a body diagonal and the U(I)-6N distance is equal to 2.29 Å.

The structure has also 16 ordered vacancy

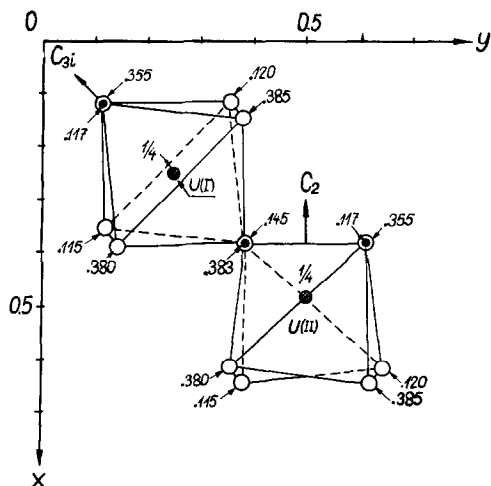


FIG. 7. The nitrogen coordination around two uranium sites:  $C_2$  and  $C_{3i}$ ; the projection on the  $xy$  plane. The closed circles are the voids  $v$ .

positions  $16c$  with one variable parameter  $v$ , which are assumed to be filled (28) as nitrogen content N(II) increases above the stoichiometric composition. The distances U(I) (or U(II))-2 N(II) are close to each other amounting approximately to 2.43 Å.

*Magnetic behavior.* Despite the large complications of the chemistry and structure of the higher nitrides it is expected that the magnetic measurements may be useful to investigate the valence state of uranium in this nonstoichiometric solid solution. The formal valency of uranium for stoichiometric  $U_2N_3$  is 4.5 if the charge  $-3$  is taken for nitrogen. By assuming that this compound is fully ionic, this indicates that the uranium ions are at least in two different valency states: either I:  $U^{4+}$  and  $U^{6+}$ , or II:  $U^{4+}$  and  $U^{5+}$ . Other possible situations are not taken into account. Thus, the problem arises whether the uranium ions favor special positions or are randomly distributed over the  $C_2$  and  $C_{3i}$  sites. Additionally, the low-point symmetry of the uranium ions produces a huge problem in the analysis of the crystal-field interaction, since as many as 15 crystal-field parameters  $A_n^m$  are required for the  $C_2$  sites and six for the  $C_{3i}$  sites. In general, the degeneracy of each electronic level of  $U^{4+}$  at the former site is completely lifted giving rise

to  $2J + 1$  singlets, while at the latter site the degeneracy is only partially lifted yielding the six Stark components. As a result the non-Kramers doublet may occur as the ground state. For ions having an odd number of electrons like, for example,  $U^{5+}$  ( $5f^1$ ) at least the twofold degenerate Stark levels must appear no matter how low a site symmetry is present. It should be borne in mind that there are three times as many  $C_2$  as  $C_{3i}$  sites in the unit cell. Hence, the total susceptibility due to the  $C_2$  and  $C_{3i}$  sites is determined from the average  $3/4\chi(C_2) + 1/4\chi(C_{3i})$ . All the above circumstances and the fact that in the actinide compounds the  $J$ -mixing effect is large make any crystal-field calculations impossible at this time.

In Case I the average effective magnetic moment is only attributed to the  $U^{4+}$  ions at the  $C_2$  and  $C_{3i}$  sites because the  $U^{6+}$  ions are diamagnetic or weakly paramagnetic. This situation may be considered as a systematic magnetic dilution of the magnetically active ions  $U^{4+}$  when the nitrogen content of the sample increases. A calculation of  $\bar{\mu}$  per  $U^{4+}$  ion leads to a substantial diminishing of this moment with an increase of the N:U

ratio (Fig. 8). If this model is true the average magnetic moment of the  $U^{4+}$  ion (composed of  $\mu(C_2)$  and  $\mu(C_{3i})$ ) markedly depends on the composition. It should be further mentioned that in the total magnetic susceptibility in this case there is a growing contribution of the temperature-independent term which originates from the nonmagnetic ions  $U^{6+}$  on the increase of the N:U ratio. So, only the narrow temperature range of the  $\chi^{-1}$  vs  $T$  curve at the lowest temperatures is considered.

In Case II the magnetically active ions are both  $U^{4+}$  and  $U^{5+}$ . It is expected for this case that the plot of  $\bar{\mu}_{\text{eff}}^2$  against the composition should show a break at the composition where all  $U^{4+}$  ions are fully oxidized into  $U^{5+}$ , e.g., for  $UN_{1.67}$  (6). So, in the range of composition above  $UN_{1.67}$  the new pair of ions,  $U^{5+}$  and  $U^{6+}$ , exists. Such a situation may be treated similarly to that in Case I and hence the value of  $\bar{\mu}_{U^{5+}}$  can be calculated in dependence on the composition (Curve b in Fig. 8). As is evident, the break in the course of the square average magnetic moment appears exactly at  $UN_{1.67}$ , thus,  $\bar{\mu}_{U^{5+}} = 1.41 \mu_B$ . It is obvious that the average susceptibilities of  $\bar{\chi}(U^{4+})$  and  $\bar{\chi}(U^{5+})$  have different temperature dependences and, if they cross each other at any temperature an inflexion point appears, in agreement with experiment. For the compositions in which  $U^{5+}$  is only diluted by  $U^{6+}$  the total susceptibility smoothly changes with temperature. In conclusion, the magnetic measurements favor Case II. But there is not sufficient experimental data to give a final solution.

On the other hand, Fujino and Tagawa (30) have recently applied a statistical model in analyzing the thermodynamic properties of  $U_2N_{3+x}$ . By fitting the theoretically derived equations to experimentally determined  $\ln p$  vs  $x$  curves, they finally have found that the model  $U_{3/2(1-x)}^{4+} U_{1/2(1+3x)}^{6+} N^{3-} + \square_{1-x}$  (where  $\square$  are the vacant  $16(c)$  lattice sites for excess nitrogen ions) gave the most satisfactory results. They were also able to estimate the upper limit of the nonstoichiometry for the  $U_2N_{3+x}$  phase which must correspond to N:U = 1.75 ( $x = 0.5$ ). In addition to this they have reported that the plot of lattice constants against composition show a dis-

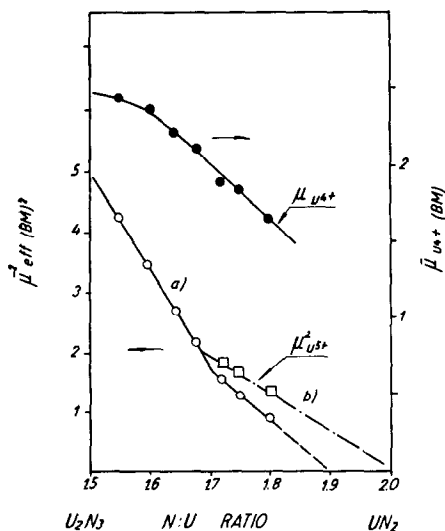


FIG. 8. Square effective magnetic moment, and average magnetic moment per  $U^{4+}$  (Case I, upper curve) as well as square average magnetic moment per  $U^{5+}$  (Case II, Curve b) of  $U_2N_{3+x}$  as a function of the N:U ratio.



continuity near N:U = 1.75, in agreement with this study.

**Ordered state.** The occurrence of the cooperative state throughout a long composition range of the uranium nitrides is rather surprising in view of the systematic change of the ground term of uranium due to the variation in its oxidizing state with the increase of nitrogen content in the sample. Unfortunately, a neutron diffraction study made at 4.2 K on bcc  $U_2N_3$  did not show any magnetic ordering (28, 31), probably due to very low values of the ordered magnetic moment of uranium in this compound. This conclusion results also from heat capacity measurements (20).

The strong crystal field, usually appearing in uranium compounds should align the magnetic moments at the sites  $C_2$  and  $C_{3i}$  along their local symmetry axes (Fig. 7), giving rise to a complex noncollinear magnetic structure similar to that of  $Er_2O_3$  (31). This magnetic structure has the same unit cell as the crystal lattice. The  $C_2$  moments are aligned along the [100] axes forming three orthogonal sets of antiferromagnetically ordered sublattices, whereas the  $C_{3i}$  moments are aligned along the [111] axes. Such a structure possesses independent antiferromagnetic arrangements of the  $C_2$  and  $C_{3i}$  site ions.

The value of the Néel temperature of  $U_2N_3$  (94 K) suggests the presence of significant exchange interactions, like in the simple uranium compounds. The magnetic interactions are diluted as nitrogen content increases and the Néel temperature varies with the relation  $T_N = 316 \times z^{3.1}$  for Case I (where  $z$  is the concentration of the  $U^{4+}$  ions). A strong magnetic exchange interaction may mix some closely spaced singlets in the case of the  $U^{4+}$  ions at the  $C_2$  sites, leading to a new ground state which carries a magnetic moment (33). This might explain, for example, the appearance of a small ordered magnetic moment for  $U^{4+}$  ions at the  $C_2$  sites.

It seemed that the complex magnetic structure, predicted for bcc uranium sesquinitride of the present work, will be sensitive to an external magnetic field. However, in the case of  $U_2N_3$  fields of up to 80 kOe did not bring

about any transition to the ferromagnetic state.

The understanding of the exchange interaction between the uranium ions with different oxidation state in such a complex crystal structure is very difficult. In the unit cell of  $U_2N_3$  each uranium ion, U(I) or U(II), coordinates always six uranium neighbors at a longer (about 3.95 Å) and six ones at a shorter distance (about 3.63 Å). Since the nitrogen atoms are coordinated with both U(I) and U(II), the overlapping of the wave functions of uranium with an intermediate ion gives rise to a strong superexchange interaction, as it probably was the case in  $U_2N_3$ . Moreover, it is generally accepted the uranium nitrides are partially covalent.

It is interesting to note that there is quite a number of rare earth oxides crystallizing in the same type of crystal structure as  $U_2N_3$  which show also antiferromagnetic properties but, in contrast to  $U_2N_{3+x}$ , have very low Néel temperatures.

### Acknowledgments

The author is indebted to Professor W. Trzebiatowski for his stimulating interest in this work.

### References

1. J. BUGL AND A. A. BAUER, *Nucl. Metal. AIME* **10**, 215 (1964).
2. H. TAGAWA, *J. Nucl. Mat.* **41**, 313 (1971).
3. P. E. LAPAT AND R. B. HOLDEN, *Nucl. Metal. AIME* **10**, 225 (1964).
4. F. MÜLLER AND H. RAGOSS, in "Thermodynamics of Nuclear Materials," p. 257. 1967 IAEA, 1968.
5. R. E. RUNDLE, N. C. BAENZIGER, A. S. WILSON, AND R. A. McDONALD, *J. Amer. Chem. Soc.* **70**, 99 (1948).
6. W. TRZEBIATOWSKI AND R. TROĆ, *Bull. Acad. Polon. Sci. Sér. Sci. Chim.* **12**, 681 (1964).
7. H. J. BERTHOLD, H. G. HEIN, AND H. REUTER, *Ber. Dt. Keram. Ges.* **50**, 111 (1973); H. J. BERTHOLD AND H. G. HEIN, *Angew. Chem.* **81**, 910 (1968).
8. W. TRZEBIATOWSKI, R. TROĆ, AND J. LECIEJEWICZ, *Bull. Acad. Polon. Sci. Sér. Sci. Chim.* **10**, 395 (1962).

9. M. ALBUTT, A. R. JUNKISON, AND R. M. DELL, *Proc. Int. Symp. Compounds Interest Nucl. Reactor Tech.* (J. T. Waber, P. Chiotti, and W. N. Miner, Eds.), p. 65 AIME, N.Y., 1964.
10. G. RAPHAEL AND C. DE NOVION, *Solid State Commun.* **7**, 791 (1969).
11. T. OHMACHI, S. NASU, AND T. KIKUCHI, *J. Nucl. Sci. Technol.* **9**, 11 (1972).
12. R. TROĆ AND D. J. LAM, *Phys. Status Solidi.* **65**, 317 (1974).
13. N. A. CURRY, *Proc. Phys. Soc.* **86**, 1193 (1965).
14. C. DE NOVION AND P. COSTA, *J. Phys.* **33**, 257 (1972).
15. M. KUZNIETZ, *Phys. Rev.* **180**, 476 (1969).
16. H. J. BERTHOLD AND C. DELLIEHAUSEN, *Angew. Chem.* **78**, 750 (1966).
17. Y. SASA AND T. ATODA, *J. Amer. Ceram. Soc.* **53**, 102 (1970).
18. C. E. PRICE AND I. H. WARREN, *Inorg. Chem.* **4**, 115 (1965).
19. F. ANSELIN, *J. Nucl. Mat.* **10**, 301 (1963).
20. J. F. COUNSELL, R. M. DELL, AND J. F. MARTIN, *Trans. Faraday Soc.* **162**, 1736 (1966).
21. H. ADACHI AND S. IMOTO, *J. Nucl. Sci. Technol.* **6**, 371 (1969).
22. H. L. DAVIS, in "Rare Earth and Actinides", p. 126 (The Institute of Physics, London, 1971).
23. J. GRUNZWEIG-GENOSSAR, M. KUZNIETZ, AND F. FRIEDMAN, *Phys. Rev.* **173**, 562 (1968).
24. H. L. DAVIS AND H. A. MOOK, in "Magnetism and Magnetic Materials" (C. D. Graham and J. J. Rhyne, Eds.), p. 1451, AIP Conf. Proc., 1971.
25. K. C. TURBERFIELD, L. PASSEL, R. J. BIRGENEAU, AND E. BUCHER, *J. Appl. Phys.* **42**, 1746 (1971).
26. C. DE NOVION, *C. R. Acad. Sci. Paris* **273**, 26 (1971).
27. J. F. COUNSELL, R. M. DELL, AND A. R. JUNKISON, *Symp. on Thermod. of Nucl. Materials with Emphasis on Solution Systems*, SM 98/30 (1967).
28. T. TOBISH AND W. HASE, *Phys. Status Solidi.* **21**, K11 (1967).
29. N. MASAKI, H. TAGAWA, AND T. TSUJI, *J. Nucl. Mat.* **45**, 230 (1972).
30. T. FUJINO AND H. TAGAWA, *J. Phys. Chem. Solids* **34**, 1611 (1973).
31. J. LECIEJEWICZ AND R. TROĆ (unpublished).
32. R. M. MOON, W. C. KOEHLER, H. R. CHILD, AND L. J. RAUBENHEIMER, *Phys. Rev.* **176**, 722 (1968).
33. B. BLEANEY, *Proc. Roy. Soc. London* **A276**, 19 (1963).