measurements have yielded conflicting, and at best, average values for the hyperfine field.

The results of this investigation together with previous results on dilute Mn in Ni are combined to separate the nearest- and next-nearest-neighbor contributions to the hyperfine field. The values obtained are $-3.2\ \text{kG}/\mu_B$ for a nearest neighbor and $-2.0\ \text{kG}/\mu_B$ for the next nearest neighbor. However, those values should be viewed with considerable caution, on account of uncertainties inherent in their derivation.

Computation of ferromagnetically and antiferromagnetically aligned Mn atoms from the long-range-order parameter S is shown to predict the bulk magnetization satisfactorily in the range $S = 0.6 - 1.0$.

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Nuclear Magnetic Resonance of ^{15}N in the Paramagnetic State of Enriched Uranium Mononitride ($U\,^{15}N$)†

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Nuclear-magnetic-resonance (NMR) measurements were made on ^{15}N in the paramagnetic state of enriched $U^{15}N$. The Knight shift K and the linewidth in $U^{15}N$ were measured under similar conditions as in previous NMR measurements on $U^{14}N$, except that in $U^{15}N$ the observed dispersion lines were distorted and broadened experimentally. Although the K values in $U^{15}N$ are slightly lower than those in $U^{14}N$, their dependence on the molar susceptibility χ_M, $K = K_0 + \alpha\chi_M$, is nearly the same, with a slope $\alpha(U^{15}N) = 3.8 \pm 0.4$ mole/emu instead of $\alpha(U^{14}N) = 4.20 \pm 0.25$ mole/emu, and with similar K_0 values. The different χ_M data in the literature and their effect on K_0 and K are attributed to variations in stoichiometry and substitutional impurities among the samples.

I. INTRODUCTION

In a previous paper,[1] continuous-wave (cw) nuclear-magnetic-resonance (NMR) measurements on ^{14}N in the paramagnetic state of uranium mononitride (UN) were reported and discussed in terms of the magnetic and electronic properties of UN. The Knight shift K and linewidth ΔH were related to the available data of the molar susceptibility χ_M, obtained by Trzebiatowski *et al.*[2] and by Albutt *et al.*[3] The two sets of data were in fair agreement with each other, and approximately represented by a Curie-Weiss behavior.

The Knight shift of ^{14}N in UN in the temperature range of 77 – 300 °K was found to be linear in χ_M,

$$^{14}K = -(31.5 \pm 3.5)\times 10^{-4} + (4.20 \pm 0.25)\chi_M, \qquad (1)$$

when the available χ_M data from Refs. 2 and 3 were used. Equation (1) has the general form of K versus χ_M in the paramagnetic state,

$$K = K_0 + \alpha\chi_M \ . \tag{2}$$

In $U^{14}N$ the free term $K_0 = -(31.5 \pm 3.5) \times 10^{-4}$ is different from the Knight shift of ^{14}N in the nonmagnetic isostructural compound ThN $[K_e = +(10.7 \pm 1.5) \times 10^{-4}]$.[4] The difference was attributed in Ref. 1 to a temperature-independent susceptibility χ_{M0} of $(1000 \pm 180) \times 10^{-6}$ emu/mole, which could not be detected in the susceptibility measurements[2,3] carried only up to 300 °K.

The linewidth of ^{14}N in UN was expressed in the form

$$\Delta H^2 = 400 + \Delta H_{\text{mag}}^2 \ , \tag{3}$$

and the magnetic contribution ΔH_{mag} was proportional to χ_M (the other contribution being the quadrupolar).

In the present paper, we report complementary results of cw NMR measurements on ^{15}N in the paramagnetic state of enriched uranium mononitride ($U^{15}N$). A possible explanation for the differences among the magnetic data for UN in the literature is discussed first.

II. SUSCEPTIBILITY OF UN

Recently, Raphael and de Novion[5] have extended the susceptibility data to the temperature range 4 – 1000 °K. They found that the magnetic susceptibility in the temperature range 60 – 550 °K is given by

$$\chi_M = \chi_{M0} + \frac{N_A n_p^2 \mu_B^2 / 3k_B}{T - \theta} \tag{4}$$

rather than by a simple Curie-Weiss behavior. The temperature (T)-dependent term arises from the $5f$-localized electrons on the uranium ions, assumed to be U^{4+} (with $5f^2$ configuration) in a simple model.[6] In this term (denoted by χ_f) n_p is the paramagnetic moment, θ is the paramagnetic Curie temperature, and the constants N_A, μ_B, and k_B are the Avogadro number, the Bohr magneton, and the Boltzmann constant, respectively. The temperature-independent term χ_{M0} arises from the conduction electrons (Pauli paramagnetism) and/or crystal-field effects (Van Vleck-type paramagnetism).

The values of χ_{M0}, n_p, and θ and some representative values of χ_M as obtained by Trzebiatowski *et al.*,[2] by Allbutt *et al.*,[3] and by Raphael and de Novion[5] are summarized in Table I. There is good agreement between the values of the first two groups (Refs. 2 and 3, denoted by TA); the susceptibility values of Raphael and de Novion[5] (denoted by RdN) are considerably lower, approximately by 300×10^{-6} emu/mole. Although the values of χ_{M0}, n_p, and θ obtained by RdN are different from those obtained by TA, Raphael and de Novion did not quote or compare the previous data to theirs. The value of χ_{M0}, estimated in Ref. 1 from the Knight-shift measurements of ^{14}N in $U^{14}N$ using the χ_M values of TA, exceeds the value quoted by RdN by $(500 \pm 180) \times 10^{-6}$ emu/mole. The lower limit of this difference is the above quoted difference between the χ_M data of RdN and of TA.

TABLE I. Comparison between the available magnetic susceptibility data for UN.

Physical quantity	UN susceptibility data		
	Ref. 2	Ref. 3	Ref. 5
Temperature range (°K)	83–300	100–300	4–1000
$10^6\chi_{M0}$ (emu/mole)	···	···	500
n_p (μ_B)	3.08	3.11	2.06
θ (°K)	−310	−325	−160
$10^6\chi_M$ (emu/mole)			
$T = 300$°K	1930	1940	1644
$T = 232$°K	2170	2160	1842
$T = 196$°K	2320	2300	1978
$T = 77$°K	3040	2990	2720

A possible explanation for the various magnetic susceptibility data of UN could be attributed to the actual stoichiometry and composition of the samples. Indeed such an explanation was recently pointed out by Moore, Fulkerson, and McElroy[7] in a paper on the transport properties of UN. In measurements of the electrical resistivity of UN, a "knee" is expected at the Neel temperature T_N. For different samples, they obtained different T_N (in the range 50–60 °K) which they attributed to minor variations in substitutional impurities and stoichiometry. It is known that minor quantities of carbon and/or oxygen replacing the nitrogen can drastically change the magnetic properties of nitrides. Replacement of the nitrogen in UN by carbon has such an effect, and $UN_{0.90}C_{0.10}$ does not order magnetically, as determined by neutron diffraction measurements.[8] A similar situation occurs by replacing the nitrogen in GdN by oxygen.[9] GdN is ferromagnetic below 69 °K, which is comparable to the ordering temperature of UN. Gambino *et al.*[9] found by neutron diffraction no magnetic ordering in $GdN_{0.95}O_{0.05}$, and came to the conclusion that the magnetization behavior of their "pure" GdN indicated the presence of a few tenths percent oxygen.

Since UN has the lowest ordering temperature (~ 53 °K) of all uranium monopnictides and monochalcogenides (see Ref. 6), the effects of actual composition are most pronounced and lead to the variations in χ_M data, as seen in Table I. The compositional variations affect the electronic properties and will primarily affect χ_{M0}. This would explain the almost constant difference, 300×10^{-6} emu/mole, in χ_M data of TA and of RdN. When these two sets of χ_M values are related to the Knight shift, they will result in different K_0 in Eq. (2). Using for K in UN (Ref. 1) the χ_M data of RdN would have resulted in a different K_0 value of $-(19 \pm 4)$

$\times 10^{-4}$ instead of the value in Eq. (1) obtained for χ_M data of TA.

III. SAMPLE AND EXPERIMENTAL DETAILS

The grey powdered sample of ^{15}N-enriched UN was provided by Dr. W. Fulkerson, coordinator of the UN research program at Oak Ridge National Laboratory. The enriched U^{15}N was prepared by R. A. Potter and T. G. Godfrey of the Metals and Ceramics Division, Oak Ridge National Laboratory, by reacting powdered depleted uranium (after hydrogenation and dehydrogenation processes) with nitrogen gas, containing at least 99% ^{15}N. The ~1500-ppm oxygen in the sample was mainly found as the secondary UO$_2$ phase, about 1% of the total sample, as in the sample of U^{14}N used in Ref. 1. The secondary UO$_2$ phase has no effect on the NMR measurements, which are indirectly affected only by the substitutional oxygen (due to changes in the electronic properties, as discussed in Sec. II).

The NMR measurements were made on a Varian variable-frequency spectrometer model V-4210A as in the case of U^{14}N.[1] Using variable (40 Hz) field modulations and various rf fields, NMR signals were detected only in the dispersion mode, as in the case of U^{14}N. However, the first derivatives of the NMR lines did not have the dip characteristic to dispersion mode derivatives (see Fig. 1 in Ref. 1) but rather resembled absorption lines. The signal-to-noise ratio was comparable to the one in U^{14}N, but definitely not better. We, therefore, were encountered with a problem in determining K and ΔH, which did not occur, for instance, for ^{31}P in the UP$_{1-x}$S$_x$ system.[10] Both ^{15}N and ^{31}P nuclei have a spin $I=\frac{1}{2}$; nevertheless, only for ^{31}P were NMR absorption lines readily observed.

The signal of ^{27}Al in a saturated solution of AlCl$_3$ in water was used as a reference for K measurements. Measurements were made at the frequencies 2.9, 4.0, and 5.8 MHz or in the corresponding ^{15}N resonance fields of about 6700, 9200, and 13400 Oe. These measurements were carried out at room temperature and at lower temperatures obtained by filling a special Dewar, fitted into the NMR probe and containing the sample, with liquid freon-22, dry ice in liquid freon-22, and liquid nitrogen (232, 196, and 77 °K, respectively.)

IV. K VERSUS χ_M: COMPARISON WITH U^{14}N

The Knight shift of ^{15}N in the paramagnetic state of U^{15}N is positive and independent of the applied magnetic field. Values of K at the four temperatures are given in Table II. These values are compared with the corresponding K values of ^{14}N in U^{14}N, as obtained in Ref. 1. The K data in U^{15}N are lower by approximately 10^{-3} with respect to the K data in U^{14}N. In general, such a difference will result in different K_0 in Eq. (2) when K is plotted versus χ_M. Since K_0 is related to χ_{M0}, which arises from the conduction electrons, the variation in K_0 could therefore be traced to variations in properties due to compositional variations.[7]

TABLE II. Temperature dependence of the nitrogen Knight shift in the paramagnetic state of U^{15}N and U^{14}N.

T(°K)	^{15}K(%) [a]	^{14}K(%) [b]
300	0.41 ± 0.02	0.50 ± 0.01
232	0.49 ± 0.02	0.59 ± 0.02
196	0.54 ± 0.03	0.65 ± 0.02
77	0.81 ± 0.03	0.94 ± 0.02

[a] Measured from the position of the maximum of the ("absorption-line-shaped") first derivatives of the dispersion lines (average over several runs at various magnetic fields).

[b] Measured from the position of the dip of the first derivatives of the dispersion lines (from Ref. 1).

The almost constant difference in K in U^{15}N and in U^{14}N could be due to a slight change in composition and carbon/oxygen impurities replacing nitrogen atoms. However, one must remember that an experimental error could also result in the nearly constant difference in K. The dispersion lines observed in both cases are remarkably different and the position for determination of K has arbitrarily been chosen. Since the lines in both cases are quite wide (see Table III for U^{15}N and Table II in Ref. 1 for U^{14}N), the choice of the line position involves an experimental error which could partially explain the constant difference in K.

Proceeding to describe ^{15}K (the Knight shift of ^{15}N in U^{15}N) in terms of χ_M, we have the two sets of χ_M data, by TA[2,3] and by RdN.[5] Both lead to the same slope α in Eq. (2), i.e.,

$$K = K_0 + (3.8 \pm 0.4)\chi_M \quad . \tag{5}$$

In Eq. (5),

$$K_0 = -(33 \pm 5) \times 10^{-4} \quad \text{for } \chi_M(\text{TA}),$$

$$K_0 = -(20 \pm 5) \times 10^{-4} \quad \text{for } \chi_M(\text{RdN}) \quad .$$

With the χ_M data of TA, Eq. (5) is

$$^{15}K = -(33 \pm 5) \times 10^{-4} + (3.8 \pm 0.4)\chi_M \ , \tag{6}$$

which is in fair agreement with Eq. (1) obtained for U^{14}N with the *same* χ_M data. This agreement is not surprising since the change in anion nuclei (from ^{14}N to ^{15}N) does not have an effect on the magnetic properties of the material. The fact that the slope α in U^{15}N is somewhat smaller than α in U^{14}N is probably due to some small changes in composition which affect the magnetic properties.

Using both slopes, α(U^{14}N) = 4.20 ± 0.25 mole/emu from Eq. (1) and α(U^{15}N) = 3.8 ± 0.4 mole/emu from Eq. (6), an average slope is obtained,

$$\alpha(\text{UN}) = 4.0 \pm 0.4 \text{ mole/emu} \ , \tag{7}$$

and it is exactly the slope obtained for K of ^{31}P versus χ_M in the UP-US solid solutions.[10]

We have previously noted[10] that the constant slope α of K versus χ_M in the UP-US solid solutions, in spite of the changes in magnetic properties, indicates that a simple RKKY mechanism is not suitable for the description of the Knight shift of anion nuclei in this system. The same conclusion could be drawn for other uranium compounds, including UN.[1]

An alternative explanation of K, based on covalent bonds with uranium neighbors, was raised for uranium compounds.[11] Such explanation was recently advanced,[12] but it does not account for the special features of the spin-lattice relaxation time in these compounds.[10,13] The descriptions of the Knight shift in UN and other uranium compounds will have to wait for a better knowledge of the electronic properties and the magnetic exchange interaction in these materials.

V. LINEWIDTH

The linewidth ΔH of ^{15}N in the paramagnetic state of enriched $U^{15}N$ shows the usual increase with increasing applied magnetic field and decreasing temperature, exhibited by other materials in the paramagnetic state. In Table III such a behavior of ΔH is shown. We measured the linewidth as the separation between half-maximum points of the "absorption-line-shaped" recorded first derivative of the dispersion line. Unlike $U^{14}N$, where a quadrupolar broadening is possible and present in Eq. (3), we expect ΔH in $U^{15}N$ to behave as the linewidth of ^{31}P in the paramagnetic state of UP. The latter is only a few (~ 5) oersteds at room temperature[10,12] and indicates that ΔH in $U^{15}N$ definitely exceeds the "real" linewidth. It is because of the experimental broadening that a relation similar to Eq. (3) could not be deduced. We therefore did not try to compare the measured ΔH to any calculation similar to the one possible in UP.[12]

TABLE III. NMR linewidth ΔH of ^{15}N in $U^{15}N$.

Frequency (MHz)	ΔH(Oe, ±2 Oe)[a] $T = 300\,°K$	$T = 77\,°K$
2.9	19	24
4.0	22	30
5.8	26	32

[a]Measured as the separation between half-maxiumum points of the (absorption-line-shaped) recorded first derivatives of the dispersion lines.

VI. CONCLUDING REMARKS

We extended previous measurements by NMR of ^{14}N in the paramagnetic state of UN containing natural nitrogen[1] to measurements on ^{15}N in enriched $U^{15}N$. This is probably the first uranium compound to be investigated by NMR on two different isotopes of a certain atom.

An explanation for the difference among various measurements of χ_M of UN was pointed out, connecting the different values with samples of different stoichiometry and/or impurity contents.

The Knight shift of ^{15}N in $U^{15}N$ is in good agreement with that of ^{14}N in $U^{14}N$, with a common slope of 4.0 ± 0.4 mole/emu in the plot of K versus χ_M. The same slope was obtained for other uranium compounds with an ordered state (such as the $UP_{1-x}S_x$ system) and showed the simple RKKY model unsuitable for the description of the Knight shift. No other known mechanism can adequately describe both the Knight shift and the spin-lattice relaxation time in these compounds, and further information on the band structure and magnetic interactions is needed before any attempt can be made at explaining the NMR results.

Some of the uncertainties in the linewidth of ^{15}N in $U^{15}N$ will probably be resolved in the planned measurements of the relaxation times of ^{15}N in $U^{15}N$.

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Theory of Inelastic Processes in Low-Energy Electron-Loss Spectroscopy. II. The Optical Potential

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The optical potential for an electron interacting with a semiinfinite dielectric is evaluated. The potential includes both bulk- and surface-plasmon contributions. It is found that the potential makes a substantial contribution to the reflectivity of the surface.

INTRODUCTION

Experimental studies of the interaction of electron beams with solids could provide valuable information about the nature of the surface of the solid. This is particularly true at low energies, where the penetration of the electron beam does not extend beyond the first few atomic layers. This penetration is inhibited by two effects: the so-called primary extinction of the incident beam and the inelastic excitation processes. In the former case, unitarity of the scattering matrix demands that as electrons are Bragg scattered out of the incident wave its amplitude must decrease. Since electrons are strongly deflected at low energies, this is an effective damping mechanism. The inelastic processes also severely limit the penetration as the electrons tend to excite bulk plasmons, surface plasmons, and phonons.

In a previous paper[1] (hereafter referred to as I) a formalism was introduced which enabled the treatment of inelastic processes in low-energy electron-loss spectroscopy by Feynman-diagram techniques. In particular, it was found that there exists an optical potential which is describable in terms of the dielectric properties of the solid. The concept of optical potentials in low-energy electron-diffraction (LEED) problems has been employed before.[2] In previous computations, however, only a bulk optical potential was utilized.[3] As demonstrated in I, the optical potential for a semiinfinite dielectric assumes a somewhat different form from that for a homogeneous dielectric. We therefore thought it worthwhile to present the computation for the optical potential for a bounded dielectric. This could then be used as an input to more sophisticated LEED or inelastic-loss-spectroscopy calculations.[4]

In Quinn's derivation of the optical potential,[3] a fully quantum-mechanical approach was employed. The self-energy of an electron moving in a dielectric medium was evaluated and an appropriate optical potential was extracted. In I, we have shown how this optical potential could be obtained directly from Maxwell's equations if semiclassical arguments are employed.[5] The optical potentials for the infinite dielectric agreed exactly. For the semiinfinite dielectric, we found a somewhat different expression which could be interpreted as the bulk potential plus a surface optical potential. The surface optical potential was taken to be localized at the surface. Physically we expect the latter potential to be confined to within a few atomic spacings of the surface.[6] As the dielectric function has no real meaning for distances smaller than this, we simply treated it as a δ function at the surface.

The evaluation of the potential in this paper closely parallels the calculation of the bulk optical potential made by Quinn.[3] The dielectric properties of the solid are taken to be those of a "Jellium" model with the same Fermi energy. Thus, it is the Lindhard dielectric constant which enters our formulas. All anisotropic effects are neglected except for the presence of a boundary. While other dielectric functions may be employed, they would undoubtedly entail additional computational effort. Therefore, as a first attempt at a crude understanding of the solid, we try this simplest case.

THEORY

Imagine the crystal to be oriented so that the outward normal is directed along the $\hat{z}$ axis. The expression derived in I for the optical potential of a semiinfinite dielectric is