The ^{15}N NMR Knight Shift and Electronic Structure of SrMoO$_{2.6}$N$_{0.4}$ in the Pauli Paramagnetic State

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The temperature-independent part (K_0) of the Knight shift, K, of SrMoO$_{2.6}$N$_{0.4}$ in the Pauli paramagnetic state as determined from the ^{15}N NMR spectrum is $K_0 = (2.87 \pm 0.01) \times 10^{-4}$, with respect to the external solid reference, (^{15}NH$_4$)$_2$SO$_4$. The fit of the spin–lattice relaxation time, T_1, to the Korringa relation confirms that nuclear spin–electron spin is the dominant relaxation mechanism. The probability density of conduction electrons, $P_f = 0.066$ Å^{-3}, and the density of electron states per unit volume per unit energy for spin-up and -down electrons at the Fermi surface, $\rho^+(\epsilon_0) = 0.87$ (eV Å^3)$^{-1}$, were deduced from the experimental results. By combining these data with the magnetic susceptibility an electronic structure model of SrMoO$_{2.6}$N$_{0.4}$ is proposed. © 1994 Academic Press, Inc.

INTRODUCTION

It has long been known that the nuclear paramagnetic resonance frequency of an atom in the metallic state is usually appreciably greater than that of the same nuclear species in nonmetallic compounds (1). This fractional shift of the nuclear magnetic resonance frequency of an atom in a metallic compound, called the Knight shift (K), is considered the amount by which the conduction electrons near the top of the Fermi surface increase the mean magnetic field strength H at the nucleus. It can be expressed in cubic symmetry as

$$K = \frac{\Delta H}{H_r} = \frac{8\pi}{3}\chi_\alpha P_f. \qquad [1]$$

In [1] $\Delta H = H_{\text{metal}} - H_r$ (r, nonmetallic reference); χ_α is the electron spin contribution to the susceptibility per atom, and P_f is the probability density for an electron at the Fermi surface evaluated at the nucleus. Diamagnetic effects can usually be neglected because they are smaller

than the Knight shift. The relationship between the Knight shift, the conduction electron contribution to the nuclear spin–lattice relaxation time, T_1, and temperature, T, was derived by Korringa (2). The inverse T_1 vs T relationship of this equation is a unique feature of the nuclear spin–electron spin relaxation mechanism and, in small molecules, for the spin–rotation interaction relaxation mechanism (3).

However, Knight shift studies are not limited to metals. The NaCl-type, metallic thorium and uranium nitrides (4–6) and carbides (7), and thorium phosphide (5, 8), were investigated by NMR, and Knight shifts were determined. The Knight shift and the NMR linewidth in the ^{14}N spectra of paramagnetic UN were measured as a function of applied magnetic field and temperature, and an exchange constant (J_{sf}) was derived. More recently, Knight shifts of numerous perovskite-related compounds have been determined. The density of states at the Fermi surface of YBa$_2$Cu$_3$O$_{7-\delta}$ was determined as a function of temperature and composition from the Knight shift of ^{89}Y (9). The ^{63}Cu Knight shift of YBa$_2$Cu$_3$O$_7$ was measured at both the Cu(1) chain and the Cu(2) plane sites by using an uniaxially aligned powder (10). The Knight shift in Tl$_2$Ba$_2$CuO$_{6+y}$ was measured by using oriented powdered samples; the spin part of the Knight shift increased with increasing hole concentration (11), and from the anisotropy of the Knight shift and spin–lattice relaxation time, an interrelation between the appearance of the superconductivity and the presence of the antiferromagnetic spin correlation was inferred. The ^{45}Sc NMR spectra of several perovskite-related Ba–Sc–Cu–O compounds were examined as a function of temperature (12); the inverse Knight shift curve had a kink at $T = 240$ K that apparently corresponded to a structural order–disorder transition. The variation of the Knight shift in La$_x$Sr$_{1-x}$VO$_3$ ($0.1 \leq x \leq 1.0$) was determined as a function of both La doping and temperature (13).

As part of our effort to characterize perovskite-related alkaline-earth transition-element oxidenitrides, we synthesized SrMoO$_{2.6}$N$_{0.4}$, determined its structure (14), and found it to exhibit metallic conductivity at room tempera-

ture. SrMoO$_{2.6}$N$_{0.4}$ is isomorphic with SrMoO$_3$, space group $Pm\bar{3}m$, with $a = 397.36(5)$ pm. Its magnetic susceptibility is almost temperature-independent from 173 K $(1.26 \times 10^{-4}$ emu mole$^{-1})$ to 300 K $(1.226 \times 10^{-4}$ emu mole$^{-1})$ and increases ~5% as the temperature is lowered to 90 K. Around 50 K a peak is apparent in the magnetic susceptibility data. It was initially suspected to result from absorbed O$_2$, but remained even after extensive purging of the system.

A ^{15}N-enriched specimen offers a distinct advantage for static NMR measurements. The nuclear spin, I, is $\frac{1}{2}$, and there is no quadrupole interaction to lead to a dominant quadrupole line splitting and additional dispersion in the electric field gradient. A ^{15}N-enriched specimen also overcomes the two problems of a low gyromagnetic ratio and minimal natural ^{15}N abundance. We therefore synthesized a ^{15}N-enriched specimen from ^{15}NH$_3$(g) and SrMoO$_4$ (14). Since the nuclear spin–electron orbit term and the spin–spin terms outside the nucleus should be negligible in the Pauli paramagnetic state, the nuclear spin–electron spin hyperfine interaction of the anions in the compounds are dominant in the temperature range studied. We report here the Knight shift of the ^{15}N NMR spectrum of this paramagnetic oxidenitride and the spin–lattice relaxation time, T_1.

EXPERIMENTAL DETAILS

The sample was prepared as described previously (14), and the composition was confirmed as SrMoO$_{2.6}$N$_{0.4}$ by neutron diffraction. It consisted of 600–700 mg of the pulverized powder confined in a cylindrical 7-mm o.d. capped zirconia container. The Knight shift was determined with respect to the external solid reference (^{15}NH$_4$)$_2$SO$_4$ (99.2 at.%; Isotec, Inc., Miamisburg, OH), which is -3.52×10^{-4} with respect to the NO$_3^-$ ion in a 5 mole liter^{-1} NH$_4$NO$_3$/2 mole liter^{-1} HNO$_3$ reference solution (15).

The ^{15}N NMR experiments were performed in a Varian Model VXR-400 spectrometer with a wideline high-power multinuclear probe at a homogeneous external field of $H_0 \approx 9.4$ T that corresponds to a Larmor frequency of $\nu_0 \approx 40.54$ MHz. The coil was ~15 mm long and had a 10-mm o.d. Spectra were detected by the pulse Fourier transformation technique with a 7.0-μsec wide 90° pulse. Both K and T_1 were measured at various constant temperatures between 173 and 373 K. Temperatures were determined with a thermocouple located inside the probe and were adjusted by flowing chilled or heated nitrogen gas, as appropriate, inside the probe. We averaged 3000 scans to attain a signal to noise ratio of 30 in the measurement of K and at least 150 scans to attain a signal to noise ratio greater than 10 in the measurement of T_1. The T_1 values

were determined by the inversion-recovery Fourier transformation technique. The recovery curves show exponential decay in the temperature range studied (see Fig. 1 for a representative curve determined at a temperature of 50°C).

RESULTS AND DISCUSSION

A typical spectrum is presented in Fig. 2. The Knight shift was found to be $(2.87 \pm 0.01) \times 10^{-4}$ and is temperature-independent within the error limits of the instrument, as are both the linewidth and the lineshape. As is apparent in Fig. 2, the linewidth is about 450 Hz and the lineshape is symmetric. K_0 expresses this temperature-independent part of the Knight shift. It is of note that the magnetic susceptibility is also temperature-independent over the same temperature range.

A plot of the relaxation time, T_1, against reciprocal temperature is shown in Fig. 3. In this figure the dashed line represents a linear least-squares fit of the data and the error bars represent the standard errors as reported by the instrument software. The solid line represents the theoretical curve derived from the Korringa equation. It is apparent that T_1 is inversely proportional to the absolute temperature and that the data are fitted well by the equation. This inverse relationship and the fit with the Korringa equation confirm the predominant role of the nuclear spin–electron spin relaxation mechanism.

We used the Knight shift value to calculate the probability density of electrons at the Fermi surface. We assumed that the conduction electron spin contribution to the magnetic susceptibility per N atom (χ_α) can be derived from the molar paramagnetic susceptibility of SrMoO$_{2.6}$N$_{0.4}$ per gram-atom of ^{15}N, 3.065×10^{-4} emu (g-at. ^{15}N)$^{-1}$ divided by Avogadro's constant. From Eq. [1] we calculated the probability density (P_f) for a conduction electron at the
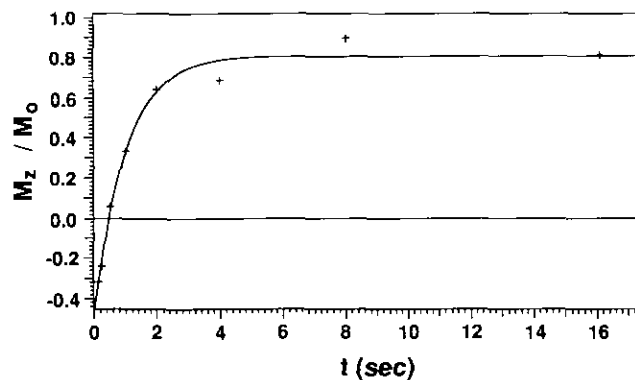

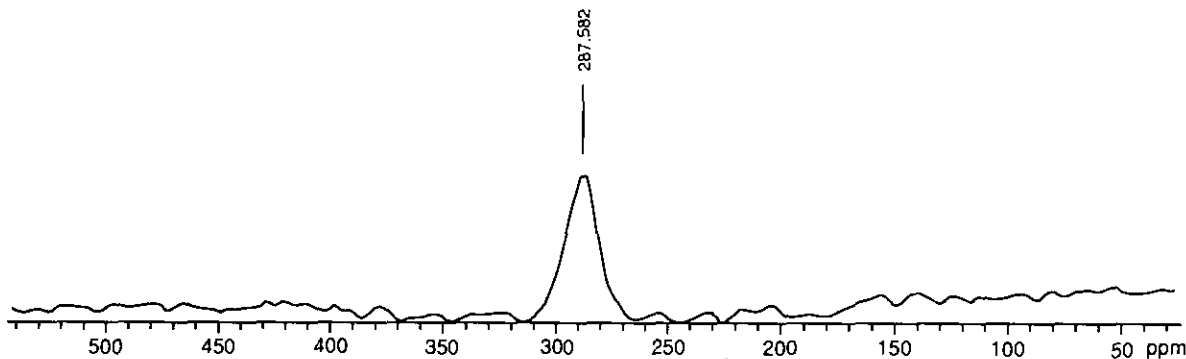FIG. 1. An inversion-recovery curve obtained for SrMoO$_{2.6}$N$_{0.4}$ at 50°C.

FIG. 2. The ^{15}N NMR spectrum of $SrMoO_{2.6}N_{0.4}$ at room temperature.

Fermi surface of our oxidenitride to be about 0.066 Å^{-3}. We estimated P_α, the probability density for a valence electron at a N nucleus at the Fermi surface in a free atom, to be 0.077 Å^{-3} by the following procedure. Using the values of $a_{3/2}$ (magnetic dipole hyperfine constant) reported in (16) for both ^{14}N and ^{15}N, 10.4507 and -14.6457 MHz, respectively, the ratio of Eq. (19) of Ref. (22), and $|\psi_{(^{14}N)}(O)|^2 = 0.094$ Å^{-3}, where $|\psi_A(O)|^2 = P_\alpha$, we calculated that for ^{15}N, $|\psi_{(^{15}N)}(O)|^2 = 0.077$ Å^{-3}. We used the value of 0.094 Å^{-3} for $|\psi_{(^{14}N)}(O)|^2$ since Goodings indicated that the calculated value of 0.1883 Å^{-3} is twice the observed value (22).

The Korringa equation (2) allows calculation of $\rho^\pm(\varepsilon_0)$, the electron state density per unit volume per unit energy for spin-up and spin-down electrons, respectively, evaluated at the Fermi surface. Assuming that $E_K^- - E_K^+ \ll \xi_0$, where $E_K^\pm$ represents the energy of the electron in spin-up or spin-down K states and ξ_0 is the energy at the Fermi surface, and assuming that the

FIG. 3. The Korringa relationship between T_1 and $1/T(K)$. The dashed line represents the experimental data fitted with a linear function; the solid line represents the theoretical curve.

difference in the properties of these two surfaces can be neglected, we express K by Eq. [2], which is derived in (17).

$$K = \frac{\gamma_e \Delta E}{\gamma_n(2I + 1)} \nu_0 \rho^+(\varepsilon_0) \frac{P_f}{P_\alpha}.\qquad [2]$$

In [2] I is a nuclear spin quantum number of ^{15}N ($\frac{1}{2}$, γ_e and γ_n are the gyromagnetic ratios of an electron and the nucleus, respectively, ΔE is the hyperfine splitting of the ground state of the free atom (29.29 MHz (1.941 $\times$ 10^{-26} J) for a ^{15}N atom) (16), and ν_0 is the Pauling radius (0.7 Å) (18). From these values we derive $\nu_0 \rho^\pm(\varepsilon_0)$ to be 7.81 $\times$ 10^{18} J^{-1} (1.251 eV^{-1}) and $\rho^\pm(\varepsilon_0) = 0.87$ (eV Å^3)$^{-1}$.

The Knight shift can also be used to study the spin polarization of the conduction electrons. The equation $K = K_0 + \alpha\chi_M$ relates K and χ_M (6). In this equation K_0 represents the Knight shift due to Pauli paramagnetism (19), χ_M is its susceptibility-temperature-dependent part, and α is a coefficient referred to as the exchange constant (J_{sf}) (19). To compare our data with those reported for metallic actinide nitride compounds, we must add $(-3.376) \times 10^{-4}$ (20) to the ^{15}N shift in $SrMoO_{2.6}N_{0.4}$ with respect to $(^{15}NH_4)_2SO_4(s)$. Our K_0 of $SrMoO_{2.6}N_{0.4}$ then becomes -5.1×10^{-5} with respect to HNO_3 (aq., 9 mole liter^{-1}). K_0 is negative in the paramagnetic state for both uranium nitride (6) and $SrMoO_{2.6}N_{0.4}$, with respect to the same HNO_3 reference, whereas K_0 for ThN is positive in a diamagnetic state (5).

The metallic, binary U-group 15 U_3E_4 and group 16 UE' compounds are ferromagnetic, while the group 15 UE, UE_2 and group 16 UOE' species are antiferromagnetic (4). The thorium compounds are diamagnetic, but the uranium compounds have ferromagnetic or antiferromagnetic type-I order and have a high transition temperature. The Knight shift can be reflective of the exchange polarization due to the conduction electrons. The excess
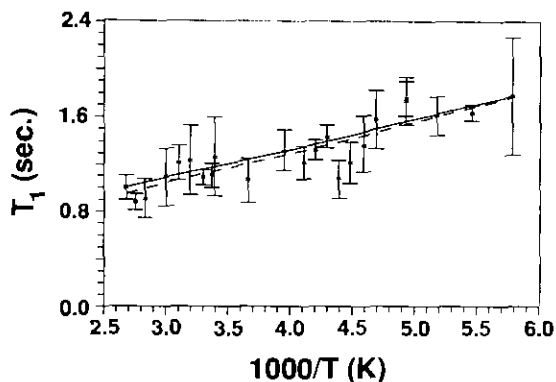
of conduction electrons with spin up over those with spin down polarizes the core electrons (21, 22). Lewis concluded that the origin of the negative K_0 in the thorium carbides could be attributed to the predominant $2p$ character of the conduction electrons (7). We presume negative K_0 results from the similar electron configuration of N^{3-} (1s^2 2s^2 2p^6) in SrMoO$_{2.6}$N$_{0.4}$ for the same reason. Bessis-Mazloum and Lefebvre-Brion (23) calculated the P_α of a free N atom and concluded that only two configurations, (1$s)^2$ (2s) (2$p)^3$ (3s) and (1s) (2$s)^2$ (2$p)^3$ (3s), could explain the hyperfine interaction on the free N atom, in good agreement with experimental results. The ($P_f/P_\alpha = 0.86$) ratio of our result indicates that the closed outer p shell in N^{3-} decreases the core polarization contribution of the conduction electrons to the Knight shift.

The magnetic susceptibility of SrMoO$_{2.6}$N$_{0.4}$ at 373 K is estimated to be 1.22×10^{-4} emu mole^{-1} by linear extrapolation from 300 K (14). Although SrMoO$_3$ and SrMoO$_{2.6}$N$_{0.4}$ are isostructural, they exhibit different magnetic properties. The magnetic susceptibility of SrMoO$_3$, 2.01×10^{-4} emu mol^{-1}, is temperature-independent over almost the entire range between liquid helium and room temperature and is slightly larger than that for SrMo O$_{2.6}$N$_{0.4}$. Bouchard and Sienko proposed a simple model for SrMoO$_3$ to interpret the Pauli paramagnetism and conductive properties, namely, that a Sr atom serves as an interstitial donor in a MoO$_3$ host structure to contribute two electrons to the collective electron assembly (24). From a comparison of the calculated and experimental volume susceptibilities they deduced that the two electrons are conduction electrons at the Fermi surface. The magnetic features suggest that at high temperatures the electronic structure of SrMoO$_{2.6}$N$_{0.4}$ is similar to that of SrMoO$_3$, except that O^{2-} is partially replaced by N^{3-}, with a resulting slight decrease of susceptibility as well as a change in the probability density (P_f) of a conduction electron at the Fermi surface. At low temperatures there is an exchange interaction between conduction and localized electrons in the metallic ion (20, 25). It would thus be desirable to measure the exchange constant by the relation between K and susceptibility (χ_M) in a low-temperature region, where the susceptibility follows the Curie Law.

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