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Nuclear Magnetic Resonance in the Metal ReO_3: ^{185}Re and ^{187}Re Knight Shifts and Spin Relaxation Rates*

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The nuclear magnetic resonances (NMR) of ^{185}Re and ^{187}Re in ReO_3 have been studied by pulsed-resonance techniques in the temperature range 1–4°K. The Knight shift, referred to aqueous $NaReO_4$, is found to be $K=(-0.25\pm0.02)\%$. The spin-lattice relaxation rates are directly proportional to the absolute temperature, with $T_1T=0.23\pm0.02$ sec °K for both isotopes. A comparison of these data with previous results for ^{183}W in the sodium tungsten bronzes Na_xWO_3 shows that the conduction-band states near the Fermi level are essentially identical in the two metals. The NMR results strongly support the view that these states are predominantly d-like.

I. INTRODUCTION

THE electronic properties of the transition-metal oxide rhenium trioxide are very similar to those of the structurally related cubic tungsten bronzes.[1] All of these materials are metals with high electrical conductivities, which at room temperature are typically only one order of magnitude smaller than in copper. Since it is unusual for an oxide to be a good metal, many experimental and theoretical attempts have been made to elucidate the electronic structures of these metallic oxides. Although detailed information about the respective band structures is still lacking, the available evidence suggests that the conduction-band states at the Fermi level are derived principally from atomic d states of the transition element. In the case of the sodium tungsten bronzes (Na_xWO_3, where $0.4<x<1.0$) this conclusion follows most directly from the results of detailed ^{23}Na and ^{183}W nuclear magnetic resonance (NMR) studies.[2–5] These investigations have provided strong support for the tungsten $5d(t_{2g})$ conduction-band model first proposed by Sienko[6,7] in which each sodium atom donates its single valence electron to a tungsten d band that is empty in the insulator WO_3. The sodium $3p$ band models of Mackintosh[8] and Fuchs,[9] on the other hand, were shown to be inconsistent with the NMR data. That the metallic character of Na_xWO_3 is not strongly dependent upon an admixture of sodium states in the conduction-band states near the Fermi level was also demonstrated by the discovery that rhenium trioxide (ReO_3) is a good metallic conductor.[7] Since rhenium has one more valence electron than tungsten, ReO_3 is isoelectronic with Na_xWO_3 in the limit $x\rightarrow1$. The two crystal structures are also very similar, both being derived from the perovskite structure. The transition-metal cations are located at the centers of the cubic unit cells and the oxygen anions at the face centers. The sodium atoms in Na_xWO_3 are distributed over the corner positions which, of course, remain unoccupied in ReO_3. The respective room-temperature lattice constants are 3.86 Å [10] ($x=1$) and 3.75 Å.[11]

In view of the above considerations one may argue that the band structures of Na_xWO_3 and ReO_3 should be essentially identical provided that the sodium atoms in the bronzes serve only as electron donors and have no appreciable effect on the lattice potential seen by the conduction electrons. Evidence for this conjecture has recently been provided by Feinleib *et al.*,[1] who found that the optical properties of ReO_3 are quite similar to those of Na_xWO_3. These authors were able to relate their ReO_3 reflectivity data to the $SrTiO_3$ band structure of Kahn and Lyendecker.[12] A qualitative fit to the experimental results was achieved by increasing both the width of the d bands as well as the strength of the spin-orbit coupling. These changes in the band parameters are consistent with the expected difference between bands derived from atomic $3d$ and $5d$ states. Because of the single conduction electron, the ReO_3 Fermi level is located in the $5d(t_{2g})$ manifold of the modified $SrTiO_3$ band structure.

The purpose of the present work was to carry out an independent comparison of ReO_3 and Na_xWO_3 based on NMR Knight shift and spin-lattice relaxation measurements. Our results for ^{185}Re and ^{187}Re in ReO_3 are

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strikingly similar to our previous[5] NMR results for ^{183}W in Na_xWO_3. Additional support is therefore provided for the view that the electronic energy bands in these metals are essentially identical and are predominantly *d*-like near the Fermi level.

II. EXPERIMENTAL METHODS

Two distinctly different samples[13] of ReO_3 were investigated. One of these (henceforth referred to as sample A) was a powder of commercial origin and was known to be slightly nonstoichiometric. The second (sample B) consisted of small, mm-sized crystals that were grown by a vapor transport technique and that are believed to be quite stoichiometric. The crystals were reduced by crushing to a powder suitable for the NMR experiments (325 mesh). The room-temperature lattice constants of both samples, as determined by powder x-ray diffraction techniques,[14] were found to be identical [$a = 3.7478(2)$ Å, where the number in parentheses is the estimated uncertainty in the last quoted digit].

The NMR measurements were made on powdered samples in the temperature range 1–4°K by means of a phase-coherent crossed-coil transient spectrometer. Radio frequency excitation was provided by a 15-kW gated class-*C* amplifier. The experiments were carried out in the frequency range 30–40 MHz. After synchronous detection, the nuclear induction signals were usually stored in a Fabri-Tek Model-1062 1024-channel signal averager, which was used in conjunction with a Fabri-Tek Model-952 high-speed digitizer. This instrument yielded a 5-bit resolution of the signal amplitude at a maximum sweep speed of 1 channel/μsec. By utilizing a sufficiently large number of repetitive sweeps, the signal-to-noise ratio could be improved sufficiently to make the experimental measurements insensitive to random errors. In some instances as, for example, in displays of resonance profiles as a function of external field strength, a PAR CW-1 boxcar integrator proved convenient.

Magnetic fields were produced by a compensated NbZr superconducting solenoid. Field strength determinations were based on NMR frequency measurements on ^{27}Al in aluminum metal at 4°K, for which the frequency-to-field (ν/H) ratio has been given as[15]

$$\nu^{(27)}(\text{metal})/H = 1.11120(2)\ \text{kHz/Oe}. \qquad (2.1)$$

Knight shifts were obtained by comparing the experimental ν/H ratios of ^{185}Re and ^{187}Re in ReO_3 against published values[16] for aqueous solutions of the reference compound $NaReO_4$. Resonance frequencies were determined from an analysis of the interference pattern produced by the nuclear and reference signals under off-resonance excitation. The zero-beat transmitter frequency was obtained from a linear interpolation of the interference versus reference-frequency data. This technique has the inherent advantage that the results are independent of the phase of the reference signal. The frequency measurements were carried out with the solenoid in the persistent current mode.

Spin-lattice relaxation times were determined in the usual way by observing the recovery of the nuclear induction signal following saturation by a comb of closely spaced rf pulses. Spin-spin relaxation times were based either on the free induction or spin-echo phase-memory decays.

III. EXPERIMENTAL RESULTS

Transient NMR signals that could be attributed to ^{185}Re and ^{187}Re were detected in both samples of ReO_3. Identification of the observed resonances was based on the different natural abundances of ^{185}Re and ^{187}Re (37.1% and 62.9%, respectively), as well as the known ratio[16] of the nuclear magnetic dipole moments ($\mu^{(187)}/\mu^{(185)} = 1.010$). The experimental observations were greatly facilitated by the relatively short spin-lattice relaxation times that are a characteristic of metals at low temperatures.

The principal distinguishing characteristic of the two ReO_3 samples was the NMR linewidth. Because of the large electric quadrupole moments of both isotopes ($Q^{(185)} \approx Q^{(187)} \approx 3b$, $I^{(185)} = I^{(187)} = \frac{5}{2}$), the linewidths are expected to be quite sensitive to lattice strains. This is demonstrated in Fig. 1, which shows a spin-echo spectrum for sample A. The nonstoichiometry of this sample is reflected in severe inhomogeneous broadening of the nuclear resonances. The two relatively narrow central resonances can be assigned to the $+\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transitions of ^{185}Re and ^{187}Re. The broad background is due to the satellite transitions which are spread over a field range of greater than 3 kOe by first-order quadrupole effects. The electric field gradients presumably arise from lattice

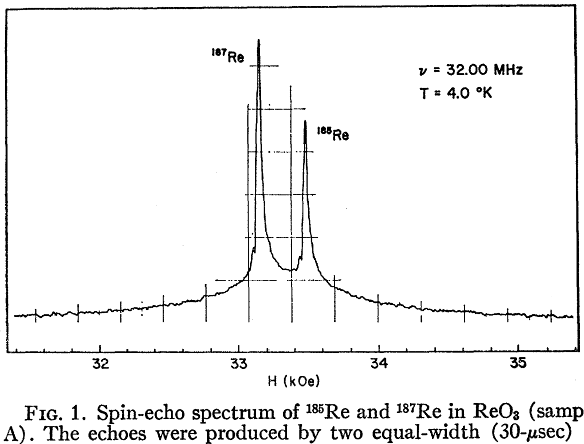

FIG. 1. Spin-echo spectrum of ^{185}Re and ^{187}Re in ReO_3 (sample A). The echoes were produced by two equal-width (30-μsec) rf pulses having a 40-μsec time separation.

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[13] Sample A was obtained from Alfa Inorganics, Inc., Beverly, Mass. Sample B was prepared by A. Ferretti, Lincoln Laboratory, MIT (see Ref. 7)

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vacancies. The echo phase-memory times of the central transitions in this sample were found to be ~600 μsec for ^{187}Re and ~720 μsec for ^{185}Re. These relaxation times were obtained with two 30-μsec-wide rf pulses in external fields near 40 kOe. Somewhat shorter phase-memory times, ~450 μsec and ~500 μsec, respectively, were obtained with pulse widths of 5 μsec.

In contrast to sample A, the contribution of quadrupole interactions to the NMR linewidths in sample B was small, as evidenced by the fact that application of a second rf pulse following the decay of the free-induction signal in a uniform external magnetic field did not lead to the formation of an echo. The free-induction decay shapes were nearly exponential. The corresponding spin-spin relaxation times at 4°K were ~38 μsec for ^{187}Re and slightly shorter for ^{185}Re. The absence of appreciable quadrupole broadening in sample B was verified by boxcar integrator measurements of the free-induction decay amplitude as a function of external magnetic field strength. Only a single narrow resonance was observed for each isotope. These results indicate that crystals of ReO_3 having a high degree of perfection can be prepared by the vapor transport process.

Measurements of the ^{185}Re and ^{187}Re ν/H ratios yielded essentially identical results for the two samples as shown in Table I. The experimental values correspond to

$$\nu^{(187)}/\nu^{(185)} = 1.01007(5), \tag{3.1}$$

which compares with the literature value[16] of 1.01026(8). The small discrepancy may, at least in part, be due to a hyperfine structure anomaly in ReO_3. Also listed in Table I are resonance shifts K derived from the present data together with the known[16] ν/H ratios in aqueous $NaReO_4$.

Because it was anticipated that it would be difficult to saturate the nuclear resonances in sample A, spin-lattice relaxation measurements were only attempted for sample B. In the range 1–4°K the relaxation rates were found to be directly proportional to the absolute temperature with

$$T_1T = 0.23(2) \text{ sec °K}. \tag{3.2}$$

No significant differences between the T_1T values for the two isotopes were detected. For a magnetic hyperfine mechanism the relaxation rates are proportional to the square of the respective gyromagnetic ratios, $\gamma_n = \mu/I\hbar$. These differ by only ~1% for the rhenium isotopes and the relaxation rates are therefore expected to be indistinguishable within the indicated experimental uncertainty.

TABLE I. Summary of Knight-shift data for ^{185}Re and ^{187}Re in ReO_3. Values in square brackets are for sample A and refer to the central transitions; all other values are for sample B.

	ν(metal)/H (kHz/Oe)	ν(reference)/H (kHz/Oe)	K(%)
^{185}Re	0.95615(4)	0.95846(9)[a]	−0.24(1)
	[0.9563(4)]		[−0.23(2)]
^{187}Re	0.96578(2)	0.96829(9)[a]	−0.26(1)
	[0.9660(2)]		[−0.24(2)]

[a] Reference 16.

TABLE II. Comparison of Knight shifts and normalized spin-lattice relaxation times for Na_xWO_3 and ReO_3. The tungsten shifts are referred to a WF_6 reference.

	K(%)	$\gamma_n^2T_1T$ (10^6 sec^{-1} °K Oe^{-2})
Na_xWO_3, $x=0.56$	−0.16(2)[a]	18.9(9)[b]
0.65	−0.18(2)	16.8(8)
0.73	−0.18(2)	12.4(6)
0.81	−0.19(1)	9.0(4)
0.89	−0.20(1)	8.4(4)
ReO_3	−0.25(2)	8.4(7)

[a] Reference 3.
[b] Reference 5.

IV. DISCUSSION

The observation of linearly increasing spin-lattice relaxation rates with increasing temperature provides evidence that the observed ^{185}Re and ^{187}Re resonance shifts and spin-lattice relaxation rates are dominated by magnetic hyperfine interactions with the ReO_3 conduction electrons. Electric quadrupole interactions with the conduction electrons are not expected to contribute significantly to the relaxation rates because the ratio Q/μ is insufficiently large.[17] Quadrupolar interactions cannot contribute to the resonance shifts because of the cubic symmetry of the rhenium sites in ReO_3.

The present results for K and $\gamma_n^2T_1T$ appear to be essentially identical to our earlier results[4,5] for the cubic sodium tungsten bronzes. This is demonstrated in Table II. It is clear that any reasonable extrapolation of the tungsten data to $x=1$ gives a normalized spin-lattice relaxation rate which differs only slightly from the rhenium relaxation rate.

A comparison of the Knight-shift data must be carried out with greater caution than is necessary for the relaxation data because of possible uncertainties in the magnitudes of the tungsten and rhenium nuclear moments. The accepted values of these moments were obtained from NMR measurements on suitable "nonmagnetic" compounds. Unfortunately, the NMR technique often leads to overestimates of nuclear moments because of paramagnetic shielding effects associated with temperature-independent (Van Vleck) orbital paramagnetism. For example, it was demonstrated recently,[18] on the basis of ENDOR experiments on the $Mn^{2+}(^6S)$ ion in various host crystals, that the ^{55}Mn moment is ~0.5% smaller than obtained previously from NMR measurements on permanganate ions. The

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Van Vleck susceptibility of the MnO_4^- complex ion responsible for this large paramagnetic shielding correction was estimated to be $\chi_{VV} \sim +70 \times 10^{-6}$ emu/mole. (This was obtained by subtracting a diamagnetic core contribution, $\chi_{dia} \sim -50 \times 10^{-6}$ emu/mole, from the experimental magnetic susceptibility of $KMnO_4$, $\chi_{expt} \sim +20 \times 10^{-6}$ emu/mole.) Since rhenium belongs to the same group of the periodic table as does manganese, the magnetic properties of the ReO_4^- ion are expected to be similar to those of the MnO_4^- ion. The magnetic susceptibility of $KReO_4$ has been reported[19] to be $\sim -30 \times 10^{-6}$ emu/mole. Combining this value with an estimated core contribution of $\sim -70 \times 10^{-6}$ emu/mole yields $\chi_{VV} \sim +40 \times 10^{-6}$ emu/mole for the perrhenate ion, which is approximately half as large as the corresponding term in the permanganate susceptibility. On the other hand, the effective orbital hyperfine coupling constant which relates the paramagnetic shielding constant to χ_{VV} may be twice as large for ReO_4^- as for MnO_4^-. It follows that the ^{185}Re and ^{187}Re nuclear moments may be in error by the same amount as was found for ^{55}Mn. The ReO_3 Knight shift may therefore be *positive*. Although its correct value cannot be determined from the available information it seems certain that it falls in the range $-0.25 < K(\%) \lesssim +0.3$.

The probable error in the ^{183}W moment is somewhat smaller. The measured magnetic susceptibility[20] of the WF_6 reference compound,[21] $\chi_{expt} \sim -53 \times 10^{-6}$ emu/mole, gives evidence that the Van Vleck susceptibility is not as large for this complex as was inferred above for the ReO_4^- ion. The fact that the paramagnetic shielding correction for WF_6 is relatively unimportant can also be seen from the trend in the ^{183}W Knight shifts[4] in Na_xWO_3 with increasing x value. The observed change in $|K|$ is in the same direction as that of the electronic specific heat.[22] The Na_xWO_3 shifts are therefore most likely *negative.*

Despite the uncertainties in the actual Knight shifts, the similarities between the NMR results for Na_xWO_3 and ReO_3 remain. Both metals are characterized by rather rapid nuclear spin-lattice relaxation rates and relatively small Knight shifts. The arguments that were used previously[5] in support of a *d*-band model for Na_xWO_3 would therefore seem to apply also to ReO_3. However, because of the possibility that the rhenium Knight shift might be positive, it is important to consider alternative conduction-band models for ReO_3. For example, it might be argued that an *s-p* band model is most realistic for rhenium trioxide in view of the fact that the effective mass ratio inferred[1] from the optical data is near unity. As shown below, however, such a conclusion is inconsistent with the NMR data.

For a nearly free-electron conduction band, which serves as a useful description for bands derived from atomic *s* and *p* states, the principal hyperfine coupling mechanism is the contact interaction. Its magnitude is proportional to the fractional *s* character or, more specifically, to the amplitude of the conduction-electron wave function at the nucleus, averaged over the Fermi surface. In the independent-electron approximation the contact Knight shift[23] and associated spin-lattice relaxation rate[24] are given, respectively, by

$$K = (2/|\gamma_e \hbar|) H_{hfs}^{(s)} \chi, \qquad (4.1)$$

$$T_1^{-1} = 2hk_B T \gamma_n^2 [N(0) H_{hfs}^{(s)}]^2, \qquad (4.2)$$

where $H_{hfs}^{(s)}$ is the effective contact hyperfine field per electron, χ is the conduction-electron spin susceptibility, k_B is Boltzmann's constant, and $N(0)$ is the bare-electron density of states at the Fermi level. These expressions may be combined to yield the well-known Korringa relation[24]

$$K^2 T_1 T = (\gamma_e/\gamma_n)^2 (\hbar/4\pi k_B). \qquad (4.3)$$

It should also be noted that the contact shift is intrinsically positive. Combining the experimental spin-lattice relaxation time (3.2) with the Korringa relation (4.3) leads to a Knight-shift estimate of $+0.47\%$ which is larger than the upper limit estimate given above. The disparity becomes even larger when the effects of electron-electron interactions are taken into account, since these tend to increase the Korringa product K^2T_1T relative to the independent-particle prediction (4.3).[25,15] In the alkali metals this product is enhanced by approximately 60%.[15] The same factor applied to ReO_3 increases the predicted contact Knight shift to $+0.60\%$.

The inconsistency of the *s-p* band model can also be demonstrated by a direct calculation of K and T_1. As a crude estimate of the hyperfine field we take the atomic 6*s* hyperfine field of rhenium[26] and reduce it by ~50% to make allowance for the effects of wave-function distortion and reduced *s* character of the conduction-band states near the Fermi level. This yields $H_{hfs}^{(s)} \sim +7 \times 10^6$ Oe. Furthermore, we assume a parabolic band occupied by one electron per atom having an effective mass equal to the free-electron mass, as suggested by the optical data. Combining the resulting values of χ and $N(0)$ with the hyperfine-field estimate according to (4.1) and (4.2) yields $K = +2.3\%$ and $T_1T = 0.009$ sec °K. The disagreement between these predictions and our experimental results falls far outside the uncer-

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tainties inherent in the analysis. Inclusion of possible electron-electron enhancement effects would again make the disparities worse. It should also be noted that ReO_3 undoubtedly has partial ionic character. The contact hyperfine field should therefore be larger than was assumed above. It is possible that *p* core-polarization contributions (if negative) could reduce the Knight shift by a small amount; the relaxation rate, however, can obviously not be reduced by the addition of noncontact hyperfine interactions. In order for the *s*-*p* band model to have any validity for ReO_3 the fractional rhenium *s* character would therefore have to be unreasonably small. Alternatively, the results might indicate a large admixture of oxygen states near the Fermi level. Although it cannot be rejected on the basis of our data, this possibility does not seem likely.

The above arguments lead to the immediate conclusion that the ReO_3 conduction-band states in the vicinity of the Fermi level have strong *d* character. A *d*-band model can account in a plausible way for the small *s* character which is required to explain the spin-lattice relaxation data. Moreover, the core-polarization and orbital-interaction mechanisms introduced by the *d* admixture do not contribute as effectively to relaxation as does the contact mechanism because the relevant *d*-hyperfine fields are typically one order of magnitude smaller than the direct contact field. The *d*-spin and *d*-orbital relaxation processes are further inhibited by interference effects which arise from the orbital degeneracy of the *d* states.[27,28]

The *d*-band model is also consistent with the small Knight shift observed in ReO_3. Qualitatively, the experimental value can be attributed to partial cancellation between positive *s*-contact plus *d*-orbital shifts and a negative *d* core-polarization shift. Such cancellation also explains the small magnitude of the Korringa product.

A quantitative partitioning of the shift and relaxation data is unfortunately not possible because the magnitudes of the various hyperfine coupling constants cannot be estimated with sufficient accuracy. It is nevertheless obvious that the NMR results are at least in qualitative agreement with the ReO_3 band structure proposed by Feinleib *et al.*[1]

Finally, one may compare the measured values of T_2 with the predicted dipolar linewidths. The calculated dipolar second moments[29] of the ^{185}Re and ^{187}Re resonances are 0.43 and 0.52 Oe^2, respectively. The corresponding free-induction decays should have nearly Gaussian shapes with relaxation times $T_2^{(185)} \sim 360\ \mu$sec and $T_2^{(187)} \sim 320\ \mu$sec. The experimental spin-spin relaxation times for sample B are one order of magnitude shorter. In addition, the relative magnitudes for the two isotopes are reversed. The most obvious sources of the additional broadening are indirect (i.e., conduction-electron coupled) exchange interactions[30,31] between unlike isotopes, and pseudodipolar interactions[31] among like as well as unlike isotopes. The exchange contribution is larger for ^{185}Re because of the greater isotopic abundance of ^{187}Re. This may account for the observation that $T_2^{(185)} < T_2^{(187)}$. In sample A the severe inhomogeneous broadening produced by quadrupole interactions makes T_2 dependent on the amplitude of the rf driving field.[32] In our experiments only the central transitions were irradiated. As a consequence, spin-spin interactions with the $m \neq \frac{1}{2}$ levels are not expected to affect strongly the phase-memory time of the $+\frac{1}{2} \leftrightarrow -\frac{1}{2}$ spin echo. The experimental observations for sample A are clearly in accord with this prediction.

V. SUMMARY

The present study has yielded strong evidence that the conduction bands of the metals ReO_3 and Na_xWO_3 are very similar. The NMR data for both metals are distinguished by spin-lattice relaxation rates that are slower than predicted for a nearly free-electron *s*-*p* conduction band, but are faster than predicted from the observed Knight shifts using the Korringa relation. The small magnitude of the Knight shifts indicates the presence of a negative hyperfine term. It may be concluded, therefore, that the conduction-band states, at least near the Fermi level, possess strong *d* character. This conclusion is in full accord with the interpretation offered by Feinleib *et al.*[1] for their ReO_3 optical-reflection data.

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