Nuclear-spin-lattice relaxation in rhenium metal

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Nuclear-spin-lattice relaxation measurements are presented for ^{187}Re in Re metal as a function of temperature. The relaxation transition probabilities were extracted from the nuclear magnetization recovery curves both in high magnetic field ($H_0 = 8$ T) nuclear-magnetic-resonance experiments and in nuclear-quadrupole-resonance ($H_0 = 0$) experiments. It is found that the dominant relaxation mechanisms is due to magnetic rather than quadrupolar hyperfine interaction with $W_M = 1.32$ T. The data are analyzed in terms of the electronic structure of Re metal. The analysis confirms that Re is a "weakly enhanced" transition metal with a nuclear relaxation rate dominated by the s-contact hyperfine interaction.

I. INTRODUCTION

Nuclear-magnetic-resonance (NMR) and nuclear-quadrupole-resonance (NQR) spectroscopies have been extensively used to investigate electronic and structural properties of metals and alloys. A large body of data of Knight shifts K, nuclear spin-lattice (T_1^{-1}) and spin-spin (T_2^{-1}) relaxation rates, and nuclear quadrupole frequencies ν_Q is now available for most metals.[1] The NMR-NQR investigation of rhenium metallic powders is complicated by the strongly inhomogeneous quadrupole interactions due to strains and defects. Recently, it was shown that NMR-NQR spectra can be obtained in Re metal in spite of a very broad line due to the inhomogeneous distribution of electric field gradients.[2] The results obtained for the spectra both in zero field and in an external magnetic field were found to agree with the values of K and ν_Q reported previously at 4.2 K in a single crystal by nuclear acoustic resonance (NAR).[3] Furthermore, it was shown[2] that measurements of nuclear spin-lattice relaxation rates are possible in principle although a correct interpretation of the data is complicated by the width of the spectrum and by the presence of unequally spaced levels.

The present study is concerned with the nuclear-spin-lattice relaxation in Re metal as a function of temperature. The primary purpose of this work is to establish the mechanism driving the spin-lattice relaxation (magnetic or quadrupolar) and to compare the results with the ones in the other transition metals to gain information about hyperfine interactions and electronic structure. A knowledge of the NMR-NQR properties of normal Re metallic powders is a prerequisite for future studies of Re small particles of interest for the intriguing physical and electronic properties and for the important technical applications, such as catalysis.[4]

II. EXPERIMENTAL DETAILS AND DATA ANALYSIS

Rhenium metal has two isotopes, ^{187}Re (62.9%, $I = \frac{5}{2}$, $\gamma/2\pi = 968.3$ Hz/Oe) and ^{185}Re (37.1%, $I = \frac{5}{2}$, $\gamma/2\pi = 958.5$ Hz/Oe). The measurements were performed close to the resonance condition of the most abundant ^{187}Re isotope although in general the resonance lines of the two isotopes overlap in part. The quadrupole coupling frequency for ^{187}Re is $\nu_Q \cong 38.5$ MHz.[2,3] The energy spacing of the nuclear levels in presence of an external magnetic field H_0 were calculated by diagonalizing the total Hamiltonian (Zeeman plus quadrupolar). In polycrystalline samples one expects a distribution of resonance frequencies whose spectral weight distribution envelope, averaged over all crystallite orientations, has a singularity for $\theta = \pi/2$ (Ref. 5) where θ is the angle between H_0 and the principal axis of the axially symmetric electric-field-gradient tensor.

The results of the numerical calculations for $\theta = \pi/2$, i.e., the hexagonal crystal axis perpendicular to H_0, are shown in Fig. 1. In Fig. 1 we also show the comparison of the exact values obtained by diagonalization of the complete Hamiltonian with the results obtained by perturbation calculations. The quadrupole perturbation on the NMR levels is treated up to second order while the Zeeman perturbation of the NQR levels is considered only in first order. The comparison shows clearly the region of mixed regime where the labeling of the levels is not defined. The pure NQR and NMR levels are labeled according to different quantization axis, namely, the principal axis of the EFG and the magnetic-field direction, respectively.[5] It should be noted that the eigenstates for $H_0 \rightarrow 0$ are pertinent to the quadrupole Hamiltonian while for a nuclear Larmor frequency $\nu_L = \gamma_N H_0 \gg \nu_Q$ they become the Zeeman levels; for intermediate fields the
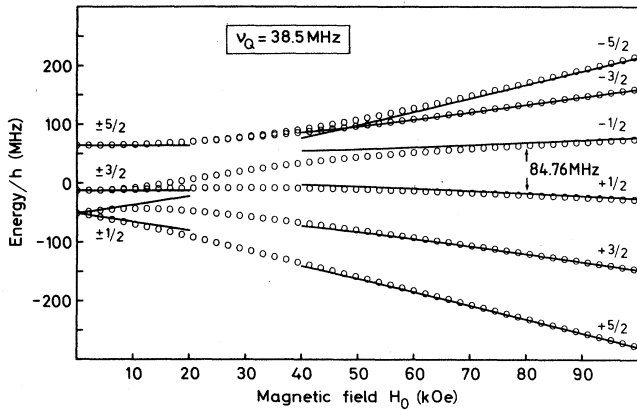
FIG. 1. (O) Exact values of the energy levels of ^{187}Re for $\theta = \pi/2$ and $\nu_Q = 38.5$ MHz. The full lines correspond to the Zeeman levels with quadrupole perturbation (right-hand side) and pure quadrupole levels with Zeeman perturbation (left-hand side). The NQR experiments were performed on the $\pm \frac{1}{2} \leftrightarrow \pm \frac{3}{2}$ transition at ν_Q, while the NMR experiments were performed on the $\pm \frac{1}{2}$ transition at 84.76 MHz ($H_0 = 8$ T).

eigenstates are a mixture of the two sets and give rise to "nonconventional" NMR spectra.[2]

In order to simplify the analysis of the relaxation measurements it was decided to work in the two following limiting conditions:

(i) NQR regime ($H_0 = 0$); observation of the $\pm \frac{1}{2} \leftrightarrow \pm \frac{3}{2}$ transition at resonance frequency ν_Q. (ii) Quadrupole perturbed NMR regime at $H_0 = 8$ T; the observed transition corresponds to the $\theta = \pi/2$ singularity of the $\pm \frac{1}{2}$ central transition. This transition was identified in the level scheme of Fig. 1 by comparing the energy spac-

ing at $H_0 = 8$ T with the one obtained from the second-order perturbation theory at $\theta = \pi/2$ (Ref. 5),

$$\nu_R = \nu_L + \frac{\nu_Q^2}{2\nu_L} = 86.88 \text{ MHz} . \tag{1}$$

The fact that the approximate value in Eq. (1) is close to the exact value in Fig. 1 indicates that at this field one can safely assume to be in the quadrupole perturbed NMR regime.

The recovery towards equilibrium of the nuclear magnetization was probed by applying one or more saturating pulses of about 4 μs followed after a delay τ by a two pulses sequence τ_p-δ-τ_p with $\tau_p \sim 4$ μs and $\delta = 20$ μs. The echo intensity was measured as a function of the delay time τ. Since the resonance lines are very broad both in NQR and in NMR experiments,[2] it is impossible to achieve the saturation of the whole line. However, the relaxation time T_1 is much shorter than the spectral diffusion time (with the exception perhaps of the lowest temperature) so that the effects of spectral diffusion can be neglected. Then by using a saturating sequence much shorter than T_1 one has initial conditions, whereby for a portion of the spectrum the irradiated levels are saturated ($\pm \frac{1}{2} \leftrightarrow \pm \frac{3}{2}$ in NQR, $+ \frac{1}{2} \leftrightarrow - \frac{1}{2}$ in NMR) with the remaining levels unchanged. Furthermore, measurements performed at different frequencies within the spectrum yielded identical results.

In order to analyze the curves for the recovery of the nuclear magnetization in terms of the relaxation transition probabilities for magnetic relaxation W_M, and for quadrupole relaxation, W_1 and W_2, one has to refer to the theoretical solutions of the master equations for $I = \frac{5}{2}$.[5,6] The solutions can be given in closed form only for the case of magnetic relaxation W_M. For the recovery of the central $\pm \frac{1}{2}$ transition in the NMR case one has[7]

$$\frac{M(t) - M(\infty)}{M(\infty)} = 0.0286 \exp(-2W_M t) + 0.178 \exp(-12W_M t) + 0.793 \exp(-30W_M t) . \tag{2}$$

For the recovery of the $\pm \frac{1}{2} \leftrightarrow \pm \frac{3}{2}$ transition line in the NQR case one has[8,9]

$$\frac{M(t) - M(\infty)}{M(\infty)} = - \frac{45}{56} \exp(-20W_M t)$$
$$- \frac{11}{56} \exp(-6W_M t) . \tag{3}$$

Both Eqs. (2) and (3) are derived for the initial conditions used in our experiments.

The general case of magnetic and quadrupolar relaxation will not be given explicitly here because it can be solved numerically only for given ratios of the relaxation transition probabilities W_M, W_1, and W_2.[9,10]

The experimental recovery curves for both NQR and NMR were tentatively fitted by assuming different values for W_M, W_1, and W_2. Although for each individual recovery curve the fit is not unique, it appears that in order to reach consistency among all the data and particularly between NMR and NQR data, it is necessary to assume $W_1 = W_2 \cong 0$ and $W_M \neq 0$. The implication of this

result is discussed in the next section. Two examples of the fits of the data obtained by using Eqs. (2) and (3) are shown in Fig. 2.

The magnetic resonance experiments were carried out on Re metallic powder with 99.999+% purity embedded in paraffin in order to eliminate spurious echo phenomena associated to magnetoacoustic excitations.[11] The NMR measurements were performed in an Oxford superconducting magnet operating at 8 T with a pulsed Fourier transform spectrometer operating at 84.75 MHz. The NQR measurements were performed with a Bruker MSL 200 spectrometer opening at 38.5 MHz.

III. RESULTS AND DISCUSSION

The experimental values of the relaxation transition probabilities W_M are shown in Fig. 3 as a function of temperature. The quantity W_M was determined by fitting the nuclear magnetization recovery according to the law in
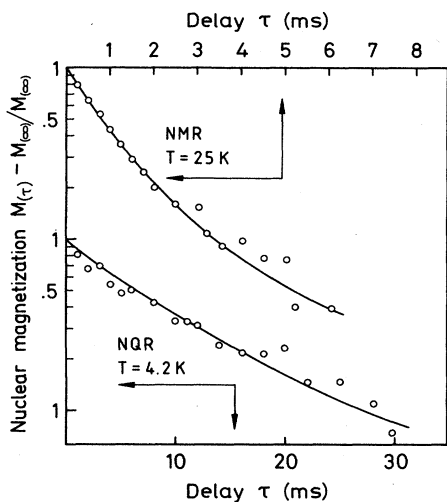
FIG. 2. Typical fits of the reduced nuclear magnetization recovery curve vs delay τ according to Eq. (2) for the NMR case ($W_M = 32$ s^{-1}) and according to Eq. (3) for the NQR case ($W_M = 6$ s^{-1}).

Eq. (2) for the NMR data at 8 T and according to Eq. (3) for the NQR data.

The nuclear-spin-lattice relaxation rate in metals is normally driven by the scattering of conduction electrons by the nuclear spins associated with the magnetic hyperfine interaction.[12] In nuclei with large quadrupole moments it is possible, in principle, to have a nonnegligible contribution from the quadrupole interaction of the nuclei with the conduction electrons.[13] Both mechanisms lead to relaxation transition probabilities which vary practically linearly with temperature. On the other hand, the quadrupole contribution due to a Raman phonon scattering by nuclei
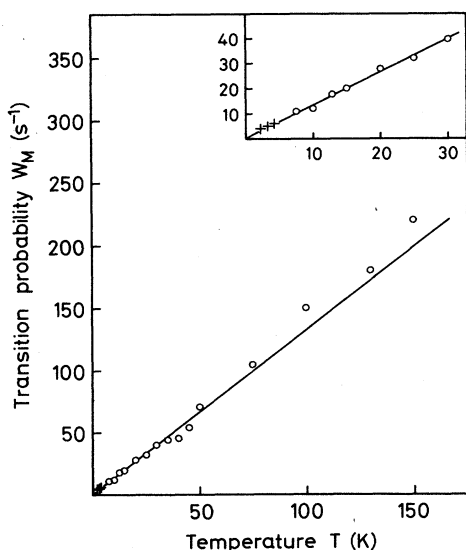

FIG. 3. Temperature dependence of the relaxation transition probability W_M in Re metal. (O) Results from NMR at $H_0 = 8$ T. ($+$) Results from NQR. The inset is an enlargement of the low-temperature region.

can be ruled out by estimating its order of magnitude by considering the T_1 values of other nuclei in insulators and scaling these values for the different quadrupole coupling strength of ^{187}Re. Furthermore, the temperature dependence of this relaxation mechanism goes as T^n with $n > 2$ at low temperature.

Unfortunately, the two Re isotopes have almost identical nuclear gyromagnetic ratios γ_N and quadrupole moments Q thus preventing an experimental determination of the origin of the relaxation from a comparison of the two isotopes. The result concerning the dominant relaxation mechanism is obtained here by considering the consistency of the fits of the nuclear recovery laws as explained in the previous section.

The values of the relaxation rate in Fig. 3 are analyzed in terms of magnetic hyperfine interactions and compared to other transition metals. The quantity which is normally considered in metals to characterize the nuclear relaxation is $T_1 T$. Recalling that in the spin-temperature approximation[5] T_1 is defined as $T_1^{-1} = 2W_M$, one has from Fig. 3

$$T_1 T = 0.38 \text{ (s K)}. \qquad (4)$$

The experimental value of $T_1 T$ will be analyzed together with the Knight shift and the magnetic susceptibility following the procedure first introduced for transition metals[14,15] and recently revisited in order to define a parametrization procedure which includes in a consistent way the effects of electron-electron interactions.[16]

By assuming a two-band model for Re with s and d bands distinguishable at the Fermi level and negligible s-d mixing we can start by a set of equations of the form[16]

$$\chi = \frac{1}{1-\alpha_s}\mu_B^2 D_s(E_F) + \frac{1}{1-\alpha_d}\mu_B^2 D_d(E_F) + \chi_{\text{orb}}, \qquad (5)$$

$$\mu_B K = \chi_s H_{\text{hf},s} + \chi_d H_{\text{hf},d} + \gamma_{\text{orb}} H_{\text{hf,orb}}, \qquad (6)$$

$$S(T_1 T)^{-1} = k(\alpha_s)K_s^2 + k(\alpha_d)K_d^2 R_d$$
$$+ [\mu_B D_d(E_F)H_{\text{hf,orb}}]^2 R_{\text{orb}}, \qquad (7)$$

where

$$S = (\gamma_e/\gamma_N)^2 \frac{\hbar}{4\pi k_B} = 5.17 \times 10^{-6} \text{ s K for } ^{187}\text{Re}.$$

A number of quantities in Eqs. (5)–(7) are either known experimentally or can be estimated theoretically. One can take for the Knight shift, $K = 1.02\%$,[3] and for the total susceptibility, $\chi = 62 \pm 6 \times 10^{-6}$ emu/mole.[1] The conduction electron susceptibility can be obtained by correcting the total value with the core diamagnetic contribution $\chi_{\text{dia}} = -55 \times 10^{-6}$ emu/mole.[17]

From a theoretical band calculation one has, for the total density of states at the Fermi level $D_{\text{tot}}(E_F)$ $= D_s(E_F) + D_d(E_F) = 11$ (Ry atom)$^{-1}$ (Ref. 18) with an estimate of the s-like contribution of $D_s(E_F)/$ $D_{\text{tot}}(E_F) = 0.1$. Furthermore, since the five d-functions are nearly equally represented at the Fermi level[18] we have:[19]

$$R_d = 0.2; \quad R_{\text{orb}} = 0.4. \qquad (8)$$

Finally, one can make a reasonable estimate of the hyperfine fields due to orbital effects and to core polarization d effects, respectively. From the estimate of $\langle r^{-3} \rangle$ for

the free atom,[20] assuming a reduction factor of 0.75 in the metal[21,22] one has

$$H_{\text{hf,orb}} = 0.7 \times 10^6 \, \text{G} .$$

Taking $|H_{\text{hf},d}| \approx |H_{\text{hf,orb}}|$ as for ^{195}Pt one ends up with values for the hyperfine fields of the same order of magnitude as found for ^{183}W in tungsten metal.[23] Also by comparison with other transition metals one can infer $\chi_{\text{orb}} = 88 \times 10^{-6}$ emu/mole.[23–25] The correction factor $k(\alpha)$ in Eq. (7) which links in a consistent way the nuclear relaxation results to the results of k and χ, was taken from the Shaw-Warren enhancement theory.[26]

There is no *a priori* reason for assuming the same functional α dependence of the correction factor for s and d electrons but, using this assumption, a consistent description of the temperature variation of K and T_1T has been obtained for Pt and Pd.[16] This dependence is given in Ref. 26 (for their parameter $\gamma = 0.25$) and taking into account exchange effects only. The best fit of Eqs. (5)–(7) with three free parameters yields

$$\alpha_s = 0.26; \quad \alpha_d = 0.25; \quad H_{\text{hf},s} = 4.9 \times 10^6 \, \text{G} , \qquad (9)$$

whereby with these values of α the correction parameter is $k(\alpha) \sim 0.8$.[26]

By substituting in Eq. (7) we can see that the relative contributions to relaxation of s, d, and orbital type are: $(T_1T)_s^{-1} = 1.48$, $(T_1T)_d^{-1} = 0.48$, and $(T_1T)_{\text{orb}}^{-1} = 0.67$, respectively, in units of $(\text{s K})^{-1}$.

On the other hand from Eq. (6) one finds that the relative contributions to the Knight shift are: $K_s = 0.31\%$, $K_d = -0.39\%$, and $K_{\text{orb}} = 1.1\%$.

In conclusion we have measured the nuclear-spin-lattice relaxation rate in Re metal for the first time and established from the recovery of the nuclear magnetization that the relaxation is dominated by the magnetic hyperfine interaction with the conduction electrons with a negligible contribution from quadrupole interactions. An analysis of the data in terms of electronic band structure indicates that Re is a weakly enhanced metal. Finally one finds that, in agreement with the case of other nearly half-filled d-band transition metals, the Knight shift is dominated by the orbital contribution while the relaxation rate is dominated by the s-direct contact term.

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[1] G. C. Carter, L. H. Bennet, and D. J. Kahan, *Progress in Materials Science* (Pergamon, New York, 1977), Vol. 20.

[2] C. Dimitropoulos, M. Maglione, and F. Borsa, Phys. Rev. B 37, 3159 (1988).

[3] J. Buttet and P. K. Baily, Phys. Rev. Lett. 24, 1220 (1970).

[4] G. C. Bond, Surf. Sci. 156, 966 (1985).

[5] A. Abragam, *Principles of Nuclear Magnetism* (Oxford Univ. Press, New York, 1961).

[6] E. R. Andrew and D. P. Tunstall, Proc. Phys. Soc. London 78, 1 (1961).

[7] W. W. Simmons, W. J. O'Sullivan, and W. A. Robinson, Phys. Rev. 127, 1168 (1962).

[8] A. C. Daniel and W. G. Moulton, J. Chem. Phys. 41, 1833 (1964).

[9] T. Rega (unpublished).

[10] M. I. Gordon and M. J. R. Hoch, J. Phys. C 11, 783 (1978).

[11] H. Alloul and C. Froidevaux, Phys. Rev. Lett. 20, 1235 (1968).

[12] J. Winter, *Magnetic Resonance in Metals* (Clarendon, Oxford, 1971).

[13] E. Haga and S. Maeda, J. Phys. Soc. Jpn. 32, 324 (1972).

[14] Y. Yafet and V. Jaccarino, Phys. Rev. 133, A1630 (1964).

[15] A. Narath and M. Weaver, Phys. Rev. 175, 373 (1968).

[16] J. P. Bucher, Ph.D. thesis, No. 747 Ecole Polytechnique Fédérale de Lausanne, 1988 (unpublished); See also J. P. Bucher and J. J. van der Klink, Phys. Rev. B 38, 11038 (1988).

[17] L. B. Mendelsohn, F. Biggs, and J. B. Mann, Phys. Rev. A 2, 1130 (1970).

[18] D. A. Papacostantopoulos, *Handbook of the Band Structure of Elemental Solids* (Plenum, New York, 1986).

[19] A. Narath, in *Hyperfine Interactions,* edited by A. J. Freeman and R. B. Frankel (Academic, New York, 1967).

[20] S. Fraga, J. Karwosky, and K. M. S. Saxena, *Handbook of Atomic Data* (Elsevier, Amsterdam, 1976), p. 481.

[21] A. M. Clogston, V. Jaccarino, and Y. Yafet, Phys. Rev. 134, A650 (1964).

[22] M. Saham, U. El-Hanany, and D. Zamir, Phys. Rev. 17, 3513 (1978).

[23] A. Narath and A. T. Fromhold, Phys. Rev. 139, A794 (1965).

[24] R. Huguenin, G. P. Pells, and D. N. Baldock, J. Phys. F 1, 281 (1971).

[25] T. Hioki, M. Kontani, and Y. Masuda, J. Phys. Soc. Jpn. 39, 958 (1975).

[26] R. W. Shaw and W. W. Warren, Phys. Rev. B 3, 1562 (1971).