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Nuclear magnetic and quadrupole resonance in metallic powders in the presence of strong quadrupole interaction: Rhenium metal

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The nuclear-magnetic-resonance and nuclear-quadrupole-resonance (NQR-NMR) spectra of ^{187}Re and ^{185}Re in a powder of rhenium metal were measured in the temperature range 5–10 K both in zero field and with an external magnetic field. The zero-field NQR spectrum is severely broadened by a nonuniform distribution of quadrupole interactions. The average quadrupole coupling frequencies measured at 5 K are, for the two isotopes, $\nu_Q=39\pm0.2$ MHz (^{187}Re) and $\nu_Q=40.8\pm0.3$ MHz (^{185}Re). The spectra obtained in the presence of an external magnetic field can be interpreted satisfactorily in terms of transitions among the eigenstates of the full Hamiltonian (Zeeman plus quadrupolar). Measurements of relaxation rates yield $T_1T=0.03$ sK, indicating a relaxation mechanism driven by the hyperfine interaction with the conduction electrons. The feasibility of NQR-NMR studies in small metal particles in the presence of strong inhomogeneous quadrupole interactions is assessed.

I. INTRODUCTION

Nuclear-magnetic-resonance (NMR) and nuclear-quadrupole-resonance (NQR) spectroscopy in metals has to be performed, generally, in polycrystalline (powder) specimens in order to allow for the penetration of the ratio frequency (rf) field. NMR and NQR signals are difficult to detect in noncubic environments when nuclei have large quadrupole moments (e.g., ^{187}Re, ^{181}Ta, . . .) particularly in powders where the electric field gradient is nonuniform due to the presence of strains and defects.[1] As a matter of fact, to the authors' knowledge, no NMR-NQR study has been reported up to date in rhenium metal. In view of the widespread interest in the physics of small metal particles[2] triggered by the intriguing physical and electronic properties and by important technical applications such as catalysis, it seems justified to renew the effort to perform NMR-NQR powder experiments in presence of strong inhomogeneous quadrupole effects.

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 Knight shift and the quadrupole coupling constant were measured at 4.2 K in a single crystal by nuclear acoustic resonance[3] (NAR). For a nucleus possessing a quadrupole moment, a conventional magnetic resonance experiment is performed in one of the two following limiting conditions:[4] zero or small external magnetic field (NQR) and strong magnetic field so that the nuclear Larmor frequency ν_L is much larger than the quadrupole coupling frequency ν_Q (quadrupole perturbed NMR). For $\nu_L<\nu_Q$ one can perform, in principle, a "nonconventional" NMR experiment. The possibility of observing a "nonconventional" NMR in polycrystalline samples was first demonstrated for $I=\frac{3}{2}$.[5] The above authors have investigated the transition between the $\pm\frac{1}{2}$ levels (quadrupole states labeling), which reduces to zero frequency when the magnetic field is reduced to zero. An attempt to observe the same transition for the nucleus ^{137}I ($I=\frac{5}{2}$ as for ^{135}Re nucleus) was unsuccessful due to the weakness of the relative transition probabilities.

In powdered Re metal a conventional NMR-NQR experiment is made difficult by the large quadrupole frequency ($\nu_Q\sim40$ MHz) and by the wide distribution of electric field gradients (efg) due to strains and defects. In this paper it is shown that by using a frequency-swept and a field-swept spin-echo technique one can observe, at low temperature, both the conventional NQR spectrum and "unconventional" NMR-NQR spectra associated to transitions among states of the full (Zeeman + quadrupolar) Hamiltonian.

II. EXPERIMENTAL

The magnetic resonance experiments were carried out on Re metallic powder with $99.999+\%$ purity. The sample was prepared by imbedding the powder in paraffin in order to eliminate the spurious echo phenomena often present in metallic powders at low temperature.[6] The equipment consisted of an electromagnet with maximum field of 22 kOe and a Bruker SXP variable-frequency pulsed spectrometer with quadrature detection. Temperature control was achieved by means of an Oxford CF 200 flow cryostat.

In order to obtain the very broad resonance spectrum (the strength of the irradiating radio-frequency field is much smaller than the spectral width, $\gamma H_1 \ll \Delta\nu$) the intensity of the echo signal following a τ_p-δ-τ_p pulse sequence was measured with a pulse length $\tau_p = 2.75$ μs and $\delta = 20$ μs. In this case the integral over a spin echo and thus its height is proportional to the amplitude of the spectrum around the measuring frequency ν_0. The full spectrum is then obtained by sweeping the static field H_0 at fixed frequency ν_0 or vice versa by sweeping the resonance frequency at fixed field.

III. RESULTS AND DISCUSSION

Figures 1 and 2 show the two types of spectra mentioned above. It should be noted that the spectra for $H_0 = 0$ and for small H_0 in Fig. 1(a) correspond to a pure NQR spectrum while the spectrum for $H_0 = 9.5$ kG in Fig. 1(b) and the field-swept spectra in Fig. 2 correspond to unconventional NMR, where the nuclear magnetic transitions take place between energy levels which are eigenstates of the full Hamiltonian, i.e., magnetic and quadrupole interactions of comparable size. Let us first consider the pure NQR spectrum in Fig. 1(a). The observed line corresponds to the $\pm\frac{1}{2} \leftrightarrow \pm\frac{3}{2}$ transition and its extreme width indicates the presence of a wide distribution of quadrupole coupling frequencies; the two lines corresponding to the two isotopes are poorly resolved. In hexagonal Re metal the electric field gradient (efg) has axial symmetry and thus the zero-field splitting of the $\pm\frac{1}{2} \leftrightarrow \pm\frac{3}{2}$ transition yields directly the quadrupole coupling frequency $\nu_Q = \frac{3}{20} e^2 qQ/h$ (eQ is the nuclear quadrupole moment and eq is the largest component of the efg tensor). Tentatively one can deduce for the average zero-field splitting a value of 39.0 ± 0.2 MHz for ^{187}Re and 40.8 ± 0.3 MHz for ^{185}Re, which compare with 38.35 ± 0.2 MHz and 40.6 ± 0.35 MHz, respectively, obtained from NAR in a single crystal.[3]

When an external magnetic field is applied, the energy levels are modified and become dependent upon the angle θ formed by the magnetic field H_0 and the direction of the greatest component $V_{ZZ} = eq$ of the efg tensor. In a polycrystalline specimen one has a distribution of resonance frequencies whose intensity distribution envelope, averaged over all crystallite orientations, has a singularity for $\theta = \pi/2$.[4,5] For applications of a small magnetic field one can use perturbation theory to calculate the modified quadrupole levels. The $\pm\frac{3}{2}$ transition is split in first order as $\Delta\nu \propto \cos\theta$ and thus is zero when the angle θ between the magnetic field and the axis of crystal symmetry is $\pi/2$. The splitting of the $\pm\frac{1}{2}$ transition, instead, has a more complicated[4] angular dependence and is nonzero for $\theta = \pi/2$. The computation of the Zeeman perturbed NQR spectrum is a formidable task involving a "powder average" of both the resonance frequency and the transition probabilities. A qualitative inspection of the transition probabilities[4] indicates, however, that the singularity at $\theta = \pi/2$ should still be present. Therefore, we will assume here that the maxima observed experimentally in the spectra correspond to such an orientation of the crystallites.

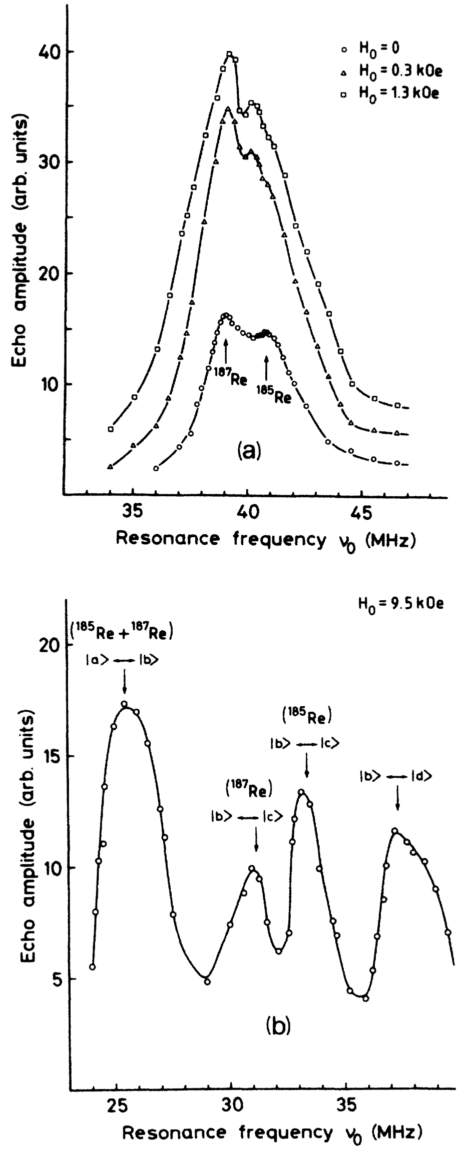

FIG. 1. ^{185}Re and ^{187}Re spectra at 5 K in a powdered sample of rhenium metal measured by the frequency-swept spin-echo method. (a) Pure NQR spectra corresponding to the $\pm\frac{1}{2} \leftrightarrow \pm\frac{3}{2}$ transition; (b) spectrum corresponding to transitions among eigenstates of the mixed Zeeman plus quadrupolar Hamiltonian (see Table I).

The spectra shown in Fig. 1(a) indicate that the application of a small magnetic field ($H_0 \leq 1.3$ kOe) does not modify substantially the zero-field NQR spectrum except for a considerable increase in signal intensity. The change in signal intensity is largely due to a variation of T_2 upon application of the external magnetic field. Values of T_2 obtained from the decay of the echo signal yield approximately: $T_2 = 12$ μs ($H_0 = 0$), $T_2 = 19$ μs ($H_0 = 0.3$ kG), and $T_2 = 28$ μs ($H_0 = 1.3$ kG).

Since the measurements in Fig. 1(a) were performed with the same delay, $\delta = 20$ μs, between the two echo-

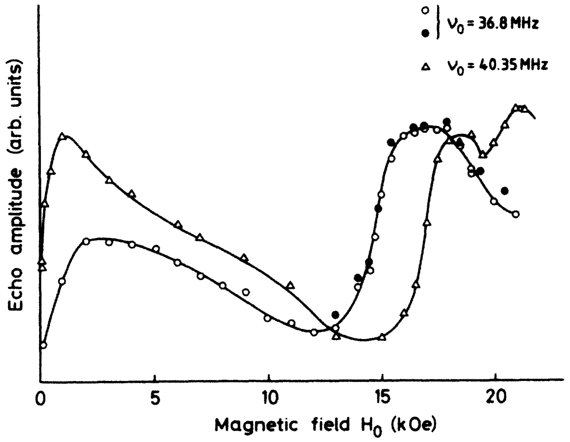

FIG. 2. Two representative ^{185}Re and ^{187}Re spectra in powdered rhenium metal measured by the field-swept spin-echo method. (○) and (△); $T=5$ K. (●); $T=7$ K. The intensity is in arbitrary units and the continuous lines are guides for the eye. The two sets of measurements at 5 and 7 K have been normalized to the same relative intensity.

forming pulses, one should renormalize the signal intensity by 1.85 and 2.6 for $H_0=0.3$ kG and 1.3 kG, respectively. The remaining differences in the renormalized signal intensity is probably related to a change in the transition probabilities. When the external magnetic field is large, the eigenstates can be obtained only by diagonalizing the full Hamiltonian for a given orientation of the external magnetic field (H_0 along the z axis) with respect to the efg symmetry axis Z and for a given ratio of the Zeeman to quadrupole interaction.[7] The energy levels were calculated numerically by diagonalizing the Hamiltonian[4] (valid for $\theta=\pi/2$ and $I=\frac{5}{2}$):

$$H=\frac{\nu_Q}{4}[I^2-I_z^2+\tfrac{1}{2}(I_+^2+I_-^2)]-\gamma H_0 I_z \,. \tag{1}$$

A typical result is shown in Fig. 3(a) for $\nu_Q=40$ MHz. The frequency swept spectrum in Fig. 1(b) shows a number of lines which can be interpreted in terms of the level scheme of Fig. 3(a). The comparison between theory and experiments is summarized in Table I. The agreement regarding the transitions $|a\rangle \leftrightarrow |b\rangle$ and $|b\rangle \leftrightarrow |c\rangle$ is satisfactory. The other resonances observed at higher frequency, instead, could not be assigned with certainty to a given isotope and/or to a given transition.

We return now to the field-swept spectrum of Fig. 2. For a given frequency of the radio-frequency (rf) field one can observe two regions where the signal is maximum, one at high field and the other at low field. By varying the measuring frequency the maxima move in opposite directions. The high-field maximum appears to result from the superposition of two maxima. One of them is easily ascribed to the $|a\rangle \rightarrow |b\rangle$ transition ($\pm\frac{1}{2}$ quadrupole states labeling) [see Fig. 3(a)]. The experimental values for the average resonance condition deduced both from the frequency-swept spectra in Fig. 1(b) and the field-swept spectra in Fig. 2 are plotted in Fig. 3(b) together with other values pertaining to spectra not shown in detail. The $|a\rangle \leftrightarrow |b\rangle$ transition reduces, as expected,[4,5] to zero frequency as $H_0 \rightarrow 0$ with an asymptotic behavior $\nu=3\gamma/2\pi H_0$, where γ is the ^{187}Re gyromagnetic ratio (practically the same as for ^{185}Re). Unfortunately, experimental points corresponding to resonance frequencies less than 20 MHz could not be obtained due to the

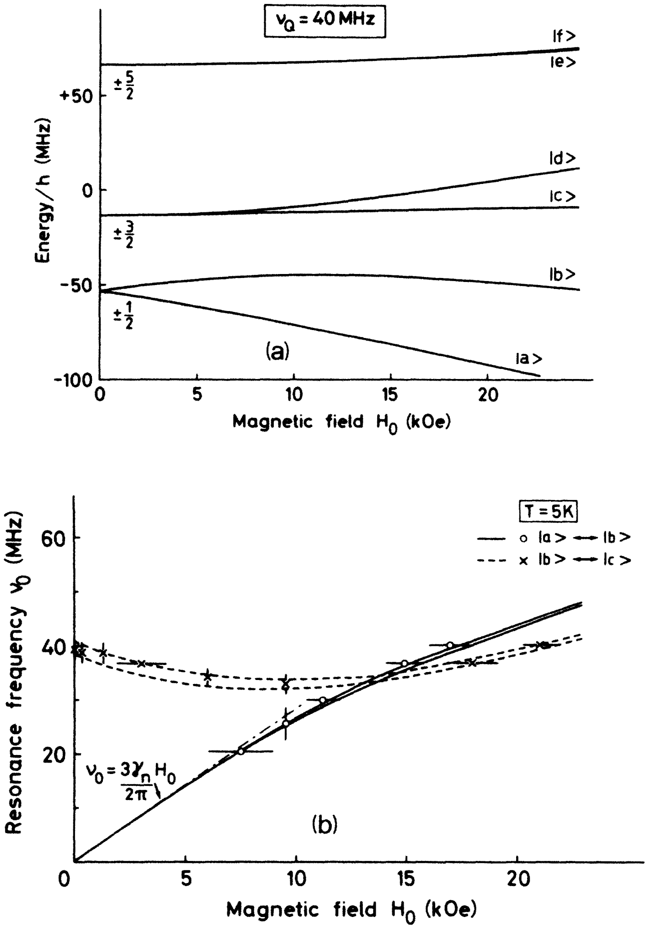

FIG. 3. (a) Energy levels of ^{187}Re for $\theta=\pi/2$. For the sake of clarity only the levels for $\nu_Q=40$ MHz are shown. The energy levels for ^{185}Re and the same ν_Q would be practically the same since $\gamma(^{185}\text{Re}) \sim \gamma(^{187}\text{Re})$. (b) Resonance frequency ν_0 plotted as a function of resonance field H_0 as deduced from the numerical results of the type shown in Fig. 3(a): the dashed line refers to the $|b\rangle \rightarrow |c\rangle$ transition; the solid line is for the $|a\rangle \leftrightarrow |b\rangle$ transition; the dotted line corresponds to the low-field asymptotic behavior of the $|a\rangle \leftrightarrow |b\rangle$ transition. The two closely spaced curves are for $\nu_Q=40.6$ MHz and $\nu_Q=38.35$ MHz, respectively, and are drawn to give an idea of the dependence of the energy levels on the quadrupole interaction. The experimental points (×) and (○) were obtained from both the frequency-swept spectra (Fig. 1) and the field-swept spectra (Fig. 2 and other spectra not shown). The values of the resonance field in the field-swept spectra were obtained from the point of maximum slope since they arise from singularities in the powder pattern (Ref. 1). All experimental points are thought to pertain to the most abundant ^{187}Re isotope.

TABLE I. Resonance frequencies ν_0 in MHz for $H_0=9.5$ kOe corresponding to the transitions between energy levels shown in Fig. 3(a). The calculated values are obtained for $\nu_Q=40.6$ MHz and $\nu_Q=38.35$ MHz, corresponding to ^{185}Re and ^{187}Re, respectively [see Fig. 1(a)]. The experimental values are obtained from the spectrum in Fig. 1(a) and are accurate within about ±0.5 MHz.

	$\vert a\rangle\leftrightarrow\vert b\rangle$		$\vert b\rangle\leftrightarrow\vert c\rangle$		$\vert b\rangle\leftrightarrow\vert d\rangle$		$\vert a\rangle\leftrightarrow\vert c\rangle$		$\vert a\rangle\leftrightarrow\vert d\rangle$	
Isotope	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.
^{185}Re	25.86	(25.60)	33.92	33.3	36.55	37.3	59.7		62.4	
^{187}Re	25.60	25.60	32.09	31.2	34.98		57.69	57.5[a]	60.58	60.5[a]

[a] Not shown in Fig. 1(b).

poor signal-to-noise ratio.

The assignment of the transition corresponding to the low-field maximum in Fig. 2 is more uncertain. If one assumes tentatively that this maximum and one of the two high-field maxima pertain both to transitions from $|b\rangle$ to $|c\rangle$ levels one obtains a reasonable agreement between the experimental points and the theoretical behavior of the resonance frequency versus resonance field [see Fig. 3(b)].

The field-swept spectra are not recommended for a precise determination of an unknown value of ν_Q since they are rather insensitive to quadrupole effects. Frequency-swept spectra are better in this respect [see Figs. 1(a) and 1(b)]. Field-swept spectra can be used to search for the signal in small metal particles and to measure the spin-lattice relaxation rate for a given transition. To check on the last point we have performed T_1 relaxation measurements for the $|a\rangle\leftrightarrow|b\rangle$ transition at $\nu_0=36.8$ MHz and $H_0=17$ kOe as a function of temperature. The measurements were performed like in conventional NMR by monitoring the recovery of the nuclear magnetization following a saturating rf pulse. The growth of the echo signal following a two-pulse sequence separated by τ from the saturating pulse is slightly nonexponential. From the initial slope of the semilogarithmic recovery plot we obtained the following results: $T_1=6$ rms at $T=5$ K, $T_1=4.2$ ms at $T=7$ K, and $T_1=2.9$ ms at $T=10$ K. A linear temperature dependence seems to hold with $T_1T=0.03$ (sK). The nuclear spin-lattice relaxation rate in metals is normally driven by the scattering of conduction electrons by the nuclear spins. The simple theory leads to the Korringa formula:[8]

$$T_1T=\frac{h}{4\pi k_B K^2}\left[\frac{\gamma_e}{\gamma_n}\right]^2 , \tag{2}$$

where k_B is the Boltzman factor, K is the Knight shift, and γ_e, γ_n are the electronic and nuclear gyromagnetic ratio, respectively. Although this formula is not directly applicable here one can use a fictitious spin $I=\frac{1}{2}$ formalism to treat the $|a\rangle\leftrightarrow|b\rangle$ transition and obtain a modified Korringa relation, where γ_n is replaced by the effective gyromagnetic ratio for the $|a\rangle\leftrightarrow|b\rangle$ transition.[9] The value of γ_{eff} can be estimated from the slope of the curve relating ν_0 to H_0 in Fig. 3(b). For $H_0\rightarrow 0$, $\gamma_{\text{eff}}/2\pi=2.9\times10^3$ Hz/Oe$=3\gamma_n/2\pi$, while for $H_0=17$ kOe one has $\gamma_{\text{eff}}/2\pi=1.5\times10^3$ Hz/Oe.

By using the latter value of $\gamma_{\text{eff}}/2\pi$ the Knight-shift value measured by NAR,[3] $K=1.03\%$, one can estimate the Korringa ratio:[1]

$$K^2T_1T\Bigg/\left[\frac{\gamma_e}{\gamma_{\text{eff}}}\right]^2\frac{h}{4\pi k_B}\sim 1.5 .$$

This ratio is almost one order of magnitude smaller than the Korringa ratio of other transition metals having comparable Knight shifts,[1,10] indicating a relaxation rate faster than expected from magnetic hyperfine interaction alone. However, it has been shown[11] that measurements of T_1 in the NQR regime may yield values for the initial decay up to an order of magnitude faster than the corresponding T_1 in the NMR regime. Thus, on the basis of this consideration and of the uncertainty about the limit of applicability of the fictitious spin-$\frac{1}{2}$ formalism one can conclude that the measured relaxation rate could still be entirely ascribed to magnetic hyperfine interactions without invoking additional contributions coming from quadrupole interaction of the nucleus with the conduction electrons.[8,11]

In conclusion, it has been shown that NQR-NMR experiments can be performed in Re metallic powder in presence of strong quadrupole effects and in spite of a very broad distribution of field gradients. For zero or small applied magnetic fields the observed spectrum corresponds to the superposition of pure NQR spectra of ^{185}Re and ^{187}Re isotopes. For higher magnetic fields ($\nu_L<\nu_Q$) the spectra are explained satisfactorily in terms of transitions among levels which are eigenstates of the full Hamiltonian although some discrepancies remain unexplained particularly regarding the signal intensities. Finally, it was shown that meaningful spin-lattice relaxation rate measurements can be performed. This kind of investigation should be of relevance to the current interest in the study of small metallic clusters.

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