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Direct acoustical measurement of nuclear spin-lattice relaxation times: Application to aluminum and tantalum

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Nuclear spin-lattice relaxation times have been measured using acoustical techniques. These techniques involve the measurement of transient effects in nuclear acoustic resonance. Two methods have been used: progressive saturation, in which the resonance line is repetitively scanned in a time short compared to the relaxation time, and, saturation and recovery, in which the resonance line is first saturated strongly and then observed a variable time later. These methods have been applied to an aluminum alloy, for which the coupling to the nucleus involves the magnetic dipole moment, and tantalum, for which the coupling involves the electric quadrupole moment.

I. INTRODUCTION

Nuclear acoustic resonance (NAR), the resonant absorption of acoustic energy by nuclear spins, has been used to study insulators,[1] semiconductors,[2] and solid[3–5] and liquid metals[6]; however, all of these experiments have been carried out with the nuclear spins in the steady-state condition. We report here on the first use of NAR to observe transient effects. Experiments have been performed for (a) coupling between the oscillatory magnetic field produced by an acoustic wave in a metal and the nuclear magnetic dipole moment, and (b) coupling between the dynamic electric field gradients produced by an acoustic wave and the nuclear electric quadrupole moment.

Previous NAR experiments have used magnetic field modulation and lock-in detection in order to record the derivative of the resonance line. In principle the spin-lattice relaxation time, T_1, can be determined from such experiments by recording the resonance signal as a function of acoustic power, i.e., through saturation measurements. In practice such experiments are difficult and time consuming to perform; moreover, the use of lock-in detection in the saturation regime does not give the true derivative of the line shape[7] so that special care is needed to extract the relaxation time from the data. As a result, NAR has not been used to measure spin-lattice relaxation times in the past. In order to avoid the problems associated with lock-in detection in the saturation regime, we have employed the method of repetitively scanning the magnetic field through the resonance and adding the signal from each scan directly in a signal averaging instrument without the use of a lock-in detector. This direct detection method has the advantage that a single sweep through the resonance line may be made in a time much shorter than is possible with lock-in detection. Theory[7] indicates that line shape changes during saturation are easier to analyze in this method, and recently, analysis and experiment[8] have shown that the signal-to-noise ratio obtained using the direct detection method is comparable to that obtained using lock-in detection. By using the direct detection method to record the NAR signal in a time shorter than T_1 it is possible to observe the transient response of the nuclear-spin system. This paper describes two such methods for measuring T_1 and gives results for aluminum and tantalum.

II. THEORY

A. Progressive saturation method

We have applied to NAR ideas previously used for NMR and ESR.[9,10] The acoustic power is set to cause partial saturation and the field is repetitively scanned through the resonance several times in a time shorter than T_1 with the signal being recorded as a single trace in a signal averager. After a delay of several T_1's in order for the spin system to return to thermal equilibrium, the experiment is repeated for signal averaging.

In order to analyze the data we follow the method[9] of Look and Locker. Designating the heights of the sequence of resonance as M_0, M_1, M_2, . . . , M_N, . . . , they show:

$$M_N = M_0\left\{1-\exp\left[\frac{-\tau}{T_1}\right]\right]\left[1-X(1-X)^N\exp\left[\frac{-N\tau}{T_1}\right]\right]\Bigg\}\Bigg/\left[1-(1-X)\exp\left[\frac{-\tau}{T_1}\right]\right] , \qquad (1)$$

where τ is the time between consecutive resonances and X is the fractional reduction in the resonance height due to one passage through the resonance. X may be calculated for the two cases of magnetic dipolar and electric quadrupolar coupling. Under the assumption that $X << 1$, the result for dipolar transitions is[7,9]

$$X_d = \frac{\pi \gamma H_1^2}{4 \nu_m H_m} \quad . \tag{2}$$

Here γ is the nuclear gyromagnetic ratio, $2H_1$ is the amplitude of the linearly polarized oscillating magnetic field producing the transition, and the magnetic field sweep is assumed to be produced by a triangular wave of peak-to-peak amplitude $2H_m$ and frequency ν_m. For our particular experimental conditions, low temperatures and shear waves along simple directions in cubic crystals, $2H_1$ is related to the acoustic strain, ϵ and the static magnetic field, H, by[11]

$$2H_1 = \epsilon H \quad . \tag{3}$$

For the $\Delta m = 2$ electric quadrupolar transition[1] we find

$$X_q = \frac{\pi A^2 [4I(I+1)-3] \, | V_{xx} - V_{yy} \pm 2i V_{xy} |^2}{80 \hbar^2 \gamma \nu_m H_m} \quad , \tag{4}$$

where I is the nuclear spin, the V_{ij} are components of the electric field gradient tensor, and $A = eQ/(2I) \times (2I-1)$ with eQ being the nuclear electric quadrupole moment.

Equation (1) was derived under the assumption that X is uniform over the sample. This assumption is not valid in the NAR case. It is common practice[1] in NAR to set up standing waves in the sample. As a first approximation we suppose that H_1 varies as $H_{10} \cos qz$ where q is the acoustic wave vector and z is the distance along the propagation direction. Then X in Eq. (1) is replaced by $X_0 \cos^2 qz$ and Eq. (1) is then averaged over the length of the sample. The calculation is rather tedious, but the result is

$$M_N = M_0 \frac{1 - e^{-\tau/T_1} [1 - X_0 (A - B) e^{-N\tau/T_1}]}{[1 + (X_0 - 2) e^{-\tau/T_1} + (X_0 + 1) e^{-2\tau/T_1}]^{1/2}} \quad , \tag{5a}$$

where

$$A = \frac{1}{4} \sum_{j=0}^{N} \binom{N}{j} \binom{2j+2}{j+1} \left(\frac{-X_0}{4} \right)^j \quad , \tag{5b}$$

$$B = \frac{1}{2} \sum_{j=0}^{N} \binom{N}{j} \left(\frac{X_0}{4} \right)^j \sum_{k=0}^{j} \binom{2j+2}{k} (-1)^k C^{j-k+1} \quad , \tag{5c}$$

$$C = 1 + \frac{2}{X_0 e^{-\tau/T_1}} \{ (1 - e^{-\tau/T_1})^{1/2} - [1 + (X_0 - 1) e^{-\tau/T_1}]^{1/2} \} (1 - e^{-\tau/T_1})^{1/2} \quad . \tag{5d}$$

Although the parameter of primary interest in the above equations is T_1, X_0 is also of interest for a comparison of theory and experiment. As we will show in a later section, X_0 may be determined from fitting the saturation data to Eqs. (5). X_0 may also be calculated from the acoustic input power and the acoustic attenuation. Equations (2) and (3) show that X_0 is related to the acoustic strain for dipolar coupling (a different relationship holds for quadrupolar coupling), but the average value of the strain amplitude ϵ may be estimated from[12]

$$\epsilon = \left(\frac{P_a}{\alpha \rho v^3 V} \right)^{1/2} \quad , \tag{6}$$

where P_a is the acoustic power input to the sample, α is the ordinary acoustic attenuation, v is the velocity of sound, ρ is the density of the material, and V is the volume of the sample containing the acoustic wave. In order to determine P_a it is necessary to determine the conversion efficiency of the particular transducer-bond combination used. The conversion efficiency and α were measured at the same temperature and field used for the NAR experiments. A comparison of X_0 values determined in these two ways is given in Sec. IV.

B. Saturation and recovery method

The analysis of the progressive saturation method is complicated because of the functional form of Eqs. (5). In order to simplify the analysis, a second method was developed. In this method the spin system is prepared in a configuration far from its equilibrium value and its recovery toward equilibrium is observed. With the acoustic power high enough to cause strong saturation the magnetic field remains at the center of the resonance for many T_1's. The field is then quickly swept off resonance. After a variable delay time the signal averager is switched on, the field is swept back through resonance, and the signal height is recorded. The entire process can be repeated for signal averaging. A measurement of signal height versus delay time allows a determination of T_1.

The signal amplitude observed at time t, $M(t)$, can be obtained from the Bloch equations.[13] The result is

$$M(t)=M_0\left[1+\left(\frac{M(t=0)}{M_0}-1\right)\exp\left(\frac{-t}{T_1}\right)\right], \quad (7)$$

where $t=0$ is taken to be the time the magnetic field is moved off resonance, and M_0 is the signal amplitude measured when the spin system is in thermal equilibrium with the lattice so that $M_0=M(t=\infty)$. Equation (7) must be averaged over the length of the sample due to the variation of the acoustic strain. This average is straightforward since M_0 is a constant, and $M(t)$ and $M(t=0)$ are merely replaced by their respective average values $\langle M(t)\rangle$ and $\langle M(t=0)\rangle$ in Eq. (7).

III. EXPERIMENTAL

The previous discussion of the NAR technique has indicated that there are two distinct cases: magnetic dipolar and electric quadrupolar coupled NAR. In general these two coupling mechanisms may be present in the same sample. However, a study of these two cases is made easier by selecting samples in which one mechanism dominates. In this study, magnetic dipolar coupling was examined in a single crystal of aluminum containing 0.87 at.% zinc, and the electric quadrupolar coupling was examined in a single crystal of tantalum.

The single crystal specimen of aluminum containing 0.87 at.% zinc was grown from high purity (99.9995%) aluminum and zinc by Materials Research Corporation. The original crystal was in the shape of a cylinder 5.6 cm long and approximately 0.93 cm in diameter with the cylinder axis being approximately 10° off the [111] crystal axis. The section of this crystal used in NAR experiments was a portion 1.05 cm long which was oriented using Laue x-ray reflection and cut to expose the (111) faces. The exposed faces were ground flat and parallel. 20-MHz fundamental-frequency ac cut-quartz transducers were bonded to these two faces using Fisher Scientific Company Nonaq stopcock grease. These two transducers were used to propagate and detect 60-MHz shear waves along the [111] crystalline axis. The zinc impurities improved the acoustic properties of the sample for NAR measurements at low temperatures by lowering the conductivity of the sample as compared to pure aluminum.

A single crystal of tantalum grown from 99.996%-pure material was obtained from Aremco Products Incorporated. The original crystal was in the shape of a cylinder 4.3 cm long and approximately 0.6 cm in diameter with the cylinder axis being approximately 1° off the [110] crystal axis. The sample was oriented, cut, and polished to expose the (110) faces. The prepared section of the crystal used in NAR measurements was 1 cm in length. Slow shear waves at 60 MHz were propagated along the [110] crystalline axis by means of 20-MHz ac cut transducers.

Tantalum is known to absorb gaseous impurities such as hydrogen, oxygen, and nitrogen easily.[14] These impurities have an effect on the NAR resonance line shape. In an attempt to remove impurities prior to experiments, the tantalum sample was heated slowly to 1000 °C in a vacuum of 10^{-6} Torr or better. The sample was kept at 1000 °C for 3 to 4 h and then slowly cooled to room temperature. This process was repeated immediately before each set of experiments. This treatment was thought to be sufficient to remove hydrogen impurities, but much higher temperatures and lower pressures are required to remove other impurities and to anneal the sample. Despite these precautions, structure was observed in the NAR line.

IV. RESULTS

A. Al-Zn

Progressive saturation experiments were performed using the ^{27}Al resonance in the Al-Zn sample. The repetitive sweeps through the resonance were achieved by using a triangular wave current to drive a sweep coil located inside the superconducting solenoid. Figure 1 shows the results of this type of measurement for several different acoustic power levels to the sample. The numbers at the right of the diagram indicate only the relative, not the absolute, power. Ten passes through the resonance are shown; $N=0-9$. These measurements were made at a temperature of 2.4 K. The triangular wave frequency was 5 Hz resulting in the time between consecutive passes through the resonance being 0.1 sec, short compared to T_1. (There are two passes through the resonance per cycle of the triangular wave.) The resonance line is seen to be sitting on a tilted background. Such a background is fairly common in NAR as there are many magnetic-field-dependent mechanisms for acoustic attenuation. Figure 1 shows the expected result that with increasing acoustic power the line saturates more quickly.

In order to obtain reliable measurements of T_1 it is important that the acoustic power and field sweep be adjusted so that the saturation of the consecutive peaks occurs at a moderate rate. Figure 2 shows such a curve from which T_1 measurements were obtained. The resonances again sit on a sloping background. The curve was recorded at a temperature of 2.2 K with the time between resonances being 0.025 sec.

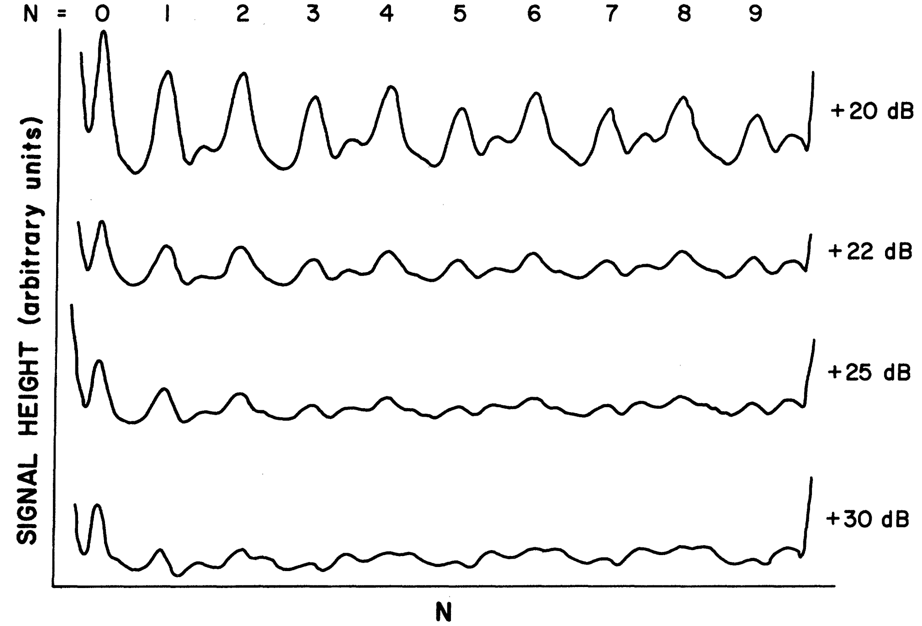

FIG. 1. ^{27}Al resonances in an Al-Zn alloy as a function of N at 2.4 K for four different acoustic powers. The numbers at the right indicate the relative, not the absolute, acoustic power. The triangular wave sweep frequency ν_m was 5 Hz. Each curve represents 64 accumulations in the signal averager.

Figure 3 shows a comparison of Eqs. (5) and the signal heights from Fig. 2. Equations (5) were plotted using the values of $T_1 = 0.72$ sec and $X_0 = 0.065$ determined from the least-squares fit to the data. This value of T_1 is in good agreement with the value of 0.82 sec expected for pure aluminum at this temperature.[15,16] Apparently the zinc impurities make at most only a small contribution to T_1. Since $X_0 << 1$, Eq. (2) applies. From Eqs. (2), (3), and (6), X_0 was calculated yielding $X_0 = 0.025$. This discrepancy in X_0 values corresponds to a factor of 1.6 difference in ϵ values which appears reasonable. It should be real-

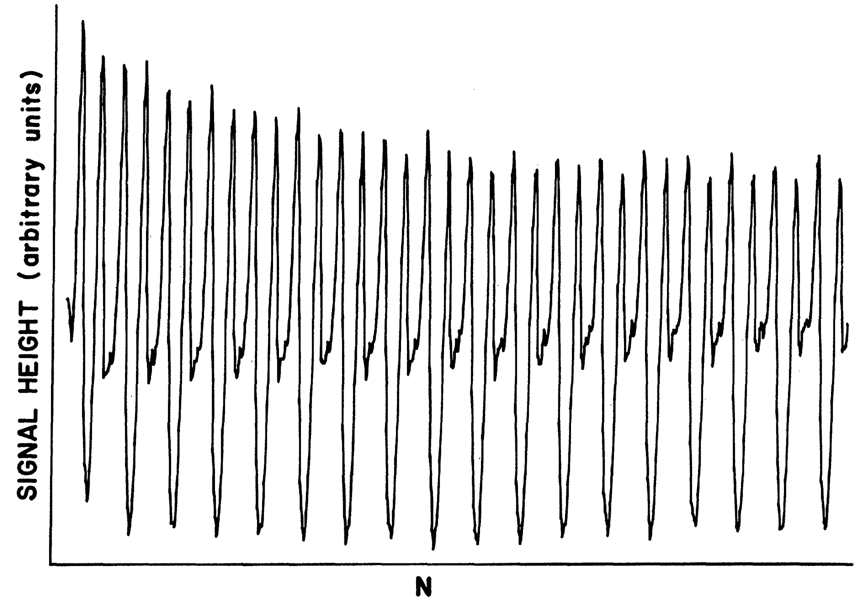

FIG. 2. ^{27}Al resonances in an Al-Zn alloy as a function of N at 2.2 K from which T_1 measurements were made with 64 accumulations in the signal averager. The triangular wave sweep frequency was 20 Hz and the peak-to-peak amplitude was 23 Oe.

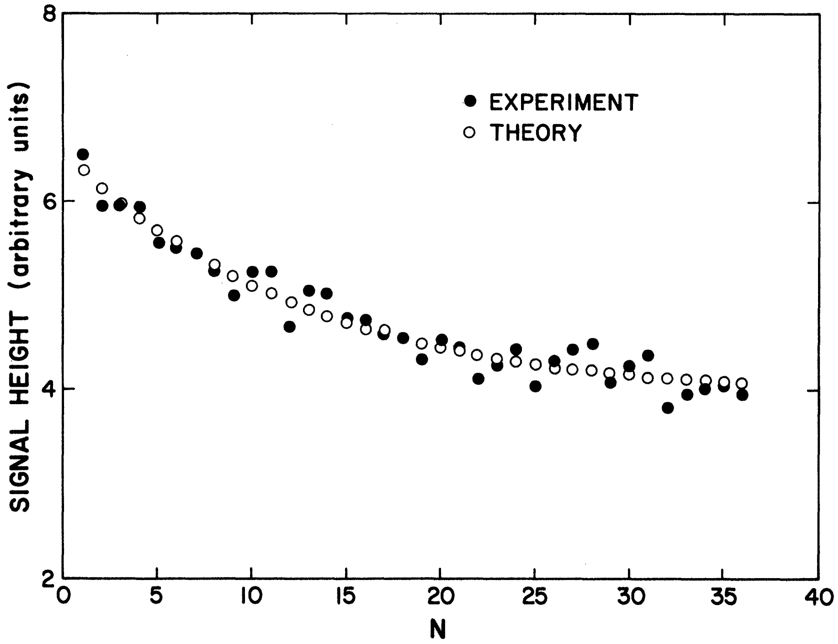

FIG. 3. Resonance heights of Fig. 2 plotted as a function of N and compared to those calculated from Eqs. (5) using $\overline{T_1} = 0.72$ sec and $X_0 = 0.065$.

ized that the determination of ϵ involves considerable uncertainty and in any case requires a careful measurement of the transducer conversion efficiency and sample attenuation. This type of experiment provides a method of directly determining the acoustic strain. If X_0 is determined from fitting the data then ϵ may be calculated through Eqs. (2) and (3).

Good measurements of T_1 have been obtained using triangular sweep frequencies of 10, 20, and 30 Hz. Equations (5) describe the data and give good results for T_1 as long as X_0 is small ($X_0 \leq 0.1$). For large $X_0 (0.6 \leq X_0 \leq 1.5)$ Eqs. (5) are not valid and it was found that Eq. (1) fits the data yielding good values of T_1. This is probably due to the fact that X is no longer proportional to H_1^2 for large X and the $\cos^2 qz$ variation in X is smoothed out so that X becomes approximately uniform along the ultrasonic beam.

Figure 4 shows data taken on Al-Zn using the saturation and recovery method. The signal heights as a function of delay times are shown. The solid line represents a computer fit of Eq. (7) to the data. This fit gives $T_1 = 0.60$ sec. The temperature was 2.6 K. Since T_1 is known to be inversely proportional to temperature in pure aluminum, a comparison of the two measurement methods is possible. The progressive saturation method gives $T_1 T = 1.58$ sec K while the saturation and recovery result is 1.56 sec K. The closeness of the two results is probably fortuitous. The result we obtain over the temperature range of 2.2–6.0 K is $T_1 T = 1.6 \pm 0.05$ sec K. The low-

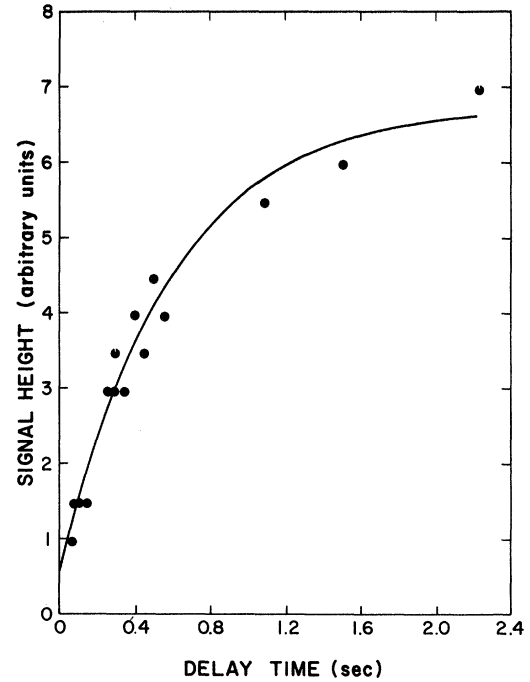

FIG. 4. ^{27}Al resonance heights as a function of delay time for the saturation and recovery method at 2.6 K. The points represent the experimental data while the solid line is the result of a computer fit of Eq. (7) to the data giving $T_1 = 0.60$ sec.

temperature value[15,16] for pure aluminum is $T_1 T = 1.80$ sec K.

B. Tantalum

Tantalum has been well studied by NAR.[14,17,18] Figure 5 shows an NAR signal for our sample obtained using the usual method of field modulation and lock-in detection. The $\Delta m = 2$ transition was observed at a temperature of 2.3 K and a frequency of 61.6 MHz. Two lines are clearly evident: a broad line and a (relatively) narrow line. Such results have been seen before in tantalum.[14] The broad line was attributed to tantalum hydride (β phase) while the narrow line was attributed to relatively pure tantalum (α phase). It seems likely that we failed to remove all of the hydrogen. Other impurities may also contribute to the broad line. In any case, the spin-lattice relaxation measurements reported below were made on the narrow line.

Figure 6 shows data taken at 2.0 K on the Ta $\Delta m = 2$ transition using the saturation and recovery method. Also shown is a computer fit of Eq. (7) to the data yielding $T_1 = 0.029$ sec.

Spin-lattice relaxation measurements have not previously been reported for tantalum. A theoretical estimate of T_1 was made using the Korringa relation.[13] The result is $T_1 = 0.073$ sec at 2.0 K. In many metals the Korringa relation yields a value of T_1 close to the experimental value at low temperature, usually well within a factor of 2, when other relaxation mechanism such as quadrupolar interactions are inefficient. Since tantalum is not a typical metal due to its strong quadrupole interactions, the value of T_1 obtained from the Korringa relation is regarded as an upper limit.

Saturation of the $\Delta m = 2$ transition causes the populations of the Ta Zeeman energy levels to depart strongly from a Boltzmann distribution. Our use of Eq. (7) to interpret the data involves the assumption that spin-spin interactions bring about a new Boltzmann distribution characterized by a spin temperature different from the lattice temperature. The above assumption is usually satisfactory for cubic solids but its validity may be questionable for Ta which has an especially large electric quadrupole moment. Residual strains in the sample may result in static quadrupole shifts of the Zeeman levels. If the energy levels are unequally spaced, the mutual spin flips needed to attain a spin temperature are somewhat suppressed. In order to guard against such complications, our measurements were made on the narrow line (in which case the quadrupolar shifts are smaller) and the first measurements occurred approximately 5 msec after saturation (a time much longer than the usual spin-spin relaxation time in solids). With these precautions, the use of Eq. (7) seems reasonable.

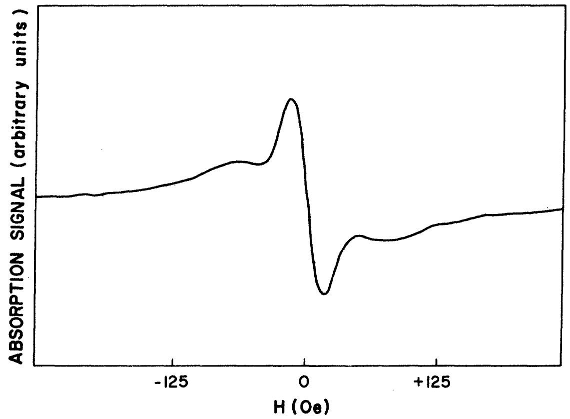

FIG. 5. Tantalum NAR $\Delta m = 2$ resonance line for the sample used for T_1 measurements. This absorption signal was recorded using field modulation and lock-in detection at a temperature of 2.3 K and an acoustic wave frequency of 61.6 MHz.

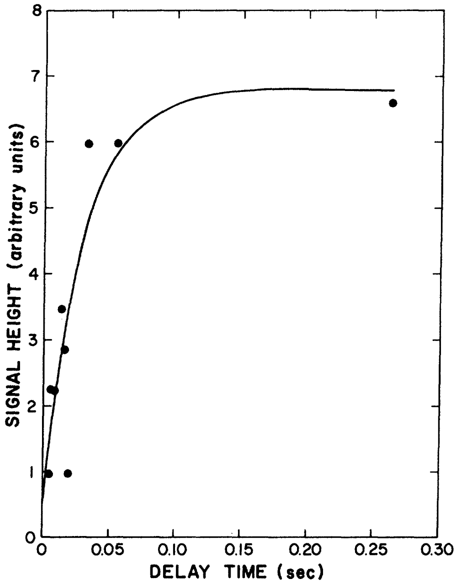

FIG. 6. Tantalum resonance heights as a function of delay time for the saturation and recovery method at 2.0 K. The points represent the data while the solid line is a computer fit of Eq. (7) to the data giving $T_1 = 0.029$ sec.

V. CONCLUSION

We have extended the NAR technique to the measurement of transient effects. Spin-lattice relaxation times can now be measured by NAR with the advantages that (a) measurements may be made on metal single crystals, and (b) measurements can be made on those materials for which the NMR signal is quite weak. Both points (a) and (b) have been demonstrated in the present paper. In addition we report a first measurement of the spin-lattice relaxation time in tantalum.

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