

Nuclear Magnetic Resonance in Solid Zinc

H. Herberg, J. Abart, and J. Voittländer

Institut für Physikalische Chemie der Universität München

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The nuclear magnetic resonance of ^{67}Zn in hexagonal close-packed Zn metal has been observed at 4.2 K by pulsed NMR with three different frequencies. The spin echo profile showed a well resolved powder pattern due to electric quadrupole interaction. The quadrupole coupling constant was determined to be $e^2 q Q/h = 12.0(4)$ MHz. The spin-spin and spin-lattice-relaxation times were measured to be $T_2 = 58 \pm 2$ ms and $T_1 = 0.45 \pm 0.2$ s, respectively. The isotropic Knight shift is found to have the value $K_{\text{iso}} = 0.1 \pm 0.05\%$.

Zinc is one of the few pure metals that have not yet been observed by nuclear magnetic resonance. This is mainly due to the low abundance (4.11%), small gyromagnetic ratio and large quadrupole interactions [1, 2] arising from the hexagonal lattice. NMR measurements in liquid zinc were published recently [3, 4]. The authors, however, were not able to detect a signal in the solid state.

In this paper we report pulsed NMR measurements in solid zinc. The sample consisted of about 15 g Zn powder ($< 32 \mu\text{m}$) of 99.999% purity. We used a high field (up to 5.2 T) low temperature (4.2 K) pulse spectrometer (Bruker SXP 4-100). The length of a 90° -pulse was appr. $12 \mu\text{s}$. Data recording was performed by a Datalab transient recorder interfaced to PDP 11 computer. The echo amplitude was measured as a function of the magnetic field (spin echo profile) at 7.8, 10.0, and 13.5 MHz. The field was calibrated against the ^{109}Ag signal in metallic silver. For measurements of T_1 and T_2 a saturation comb and a 90° - τ - 180° pulse sequence were used, respectively. The experimental details are described elsewhere [5].

Figure 1 shows a 90° – 180° spin echo sequence (one scan). The small echo width of about $25 \mu\text{s}$ comes from the large inhomogeneous distribution of Knight shifts. Since at $T = 4.2$ K, $T_2 = 58 \pm 2$ ms is exceptionally long, the observation of the echo is not affected by long magnetoacoustic ringing. The large value of T_2 presumably arises from strong quadru-

pole interaction suppressing spin flip processes of neighboring spins [6].

The echo intensity vs pulse separation dependence was exponential and thus corresponding to a Lorentzian line shape.

Preliminary T_1 measurements gave at $T = 4.2$ K, $T_1 = 0.45 \pm 0.2$ s, which is a typical order of magnitude in metallic systems.

The spin echo profile at 7.81 MHz is shown in Fig. 2, where each point results from 1000 scans of a single echo. The spectrum is of $I = 5/2$ type two pairs of satellites and the central line split by second order quadrupole effects. The quadrupole frequency

$$\nu_Q = \frac{e^2 q Q}{h} \left[\frac{3}{2I(2I-1)} \right]$$

being low compared to the Zeeman frequency ν_R , we need not consider higher order perturbation terms. At higher frequencies the spectra also show a step [7] in the middle of the central line.

To derive the separation of the outer and inner satellite singularities

$$\begin{aligned} \nu(-3/2 \longleftrightarrow -5/2) - \nu(5/2 \longleftrightarrow 3/2) \\ = 2 \nu_Q(1 - \eta), \\ \nu(-1/2 \longleftrightarrow -3/2) - \nu(3/2 \longleftrightarrow 1/2) \\ = \nu_Q(1 - \eta) \end{aligned}$$

we applied the theoretical expressions deduced by Jones et al. [7] to our spectra, which later were generalized [8, 9] to the case of non zero asymmetry parameter η .

We adopted the procedure of v. Meerwall et al. [10] to determine the theoretical singularity which does not coincide with the experimental maximum in dipole broadened spectra.

If we assume $\eta = 0$, which is consistent with measurements with perturbed angular techniques [11] Mößbauer effect measurements [1], and plausibility considerations, we deduce a quadrupole coupling constant of $e^2 q Q/h \approx 12.0(4)$ MHz. This agrees well with the Mößbauer results, but is at variance with NQR experiments, which give $e^2 q Q/h = 13.620(8)$ MHz [2].

If we accept, however, the measured NQR frequency [2]

$$\begin{aligned} \nu(\pm 5/2 \longleftrightarrow \pm 3/2) = 4.086 \text{ MHz} \\ = 2 \nu_Q(1 - 0.2037 \eta^2), \end{aligned}$$

the satellite separation in Fig. 2 can only be explained with $\eta = 0.15 \pm 0.05$, leading to $\nu_Q = 2.052$ MHz. Unfortunately, neither the $(\pm 1/2 \longleftrightarrow$

Reprint requests to Prof. Dr. J. Voittländer, Institut für Physikalische Chemie der Universität München, Sophienstr. 11, D-8000 München 2.

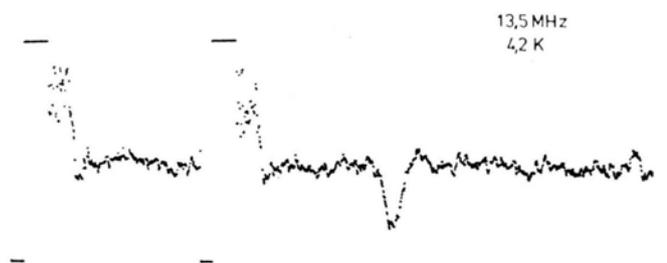


Fig. 1. Single scan of a 90° - τ - 180° spin echo pulse sequence at 5.0172 T of ^{67}Zn in zinc metal.

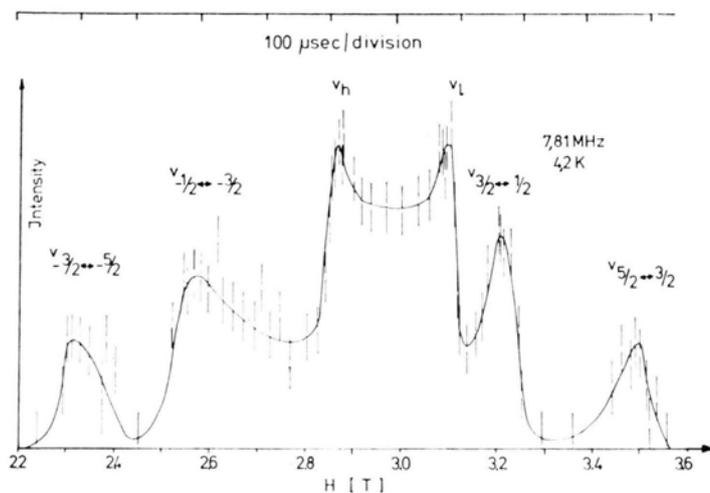


Fig. 2. Plot of the observed ^{67}Zn spin echo profile at a constant frequency of 7.81 MHz in zinc metal.

$\pm 3/2$ - NQR transition has been measured, nor the Mößbauer spectrum is very sensitive to values of $\eta \lesssim 0.15$ [12]. The NMR spectrum cannot give any further information as no shoulders or steps [8, 9] could be observed.

In any case it is possible to derive the Knight shift from the frequency dependence of the central transition:

$$K_{\text{iso}} = 0.1 \pm 0.05\%, \quad K_{\text{ax}} \approx 0.$$

At present it is impossible to evaluate the Knight shift more accurately because of the large error bars (Fig. 2), the broad echo profile and the uncertainty of the exact value of η . Nevertheless K_{iso} is in

good agreement with the estimated $K_{\text{iso}} \approx 0.2\%$ [13]. In comparison with the case of liquid zinc ($K_{\text{iso}}^{\text{m.p.}} = 0.336\%$) one may assume K to show either an unusually large drop at the melting point or a considerable temperature dependence as in the case of solid cadmium.

Further measurements are in progress.

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