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Temperature dependence of the nuclear quadrupole coupling and relaxation time of ^{25}Mg in Mg metal

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Abstract. The temperature dependences of the quadrupole coupling (e^2qQ/h) and relaxation time (T_1) for ^{25}Mg in metallic magnesium have been studied in the range 150 K to 400 K. The Korringa product $T_1T = 74(2)$ s K.

1. Introduction

The calculation of the standard nuclear magnetic properties of metals presents a well defined challenge to band structure theorists. Specifically, a good band structure should be the basis for reproducing the Knight shift, the longitudinal relaxation time and, for non-cubic metals, the nuclear quadrupole coupling. Recently there has been some interest in the possibility of a universal temperature dependence for the nuclear quadrupole coupling.

Magnesium has a hexagonal close-packed structure which implies an axially symmetric electric field gradient tensor; i.e. zero asymmetry parameter at the nuclear site. The isotope ^{25}Mg has spin $I = 5/2$, so that apart from the central $(1/2, -1/2)$ transition there are four satellite transitions which generally survive in a powder spectrum only as weak singularities corresponding to $\theta = 90^\circ$ (where θ is the angle between the c axis and the magnetic field). For the case of the zero asymmetry parameter the spacing between the satellite peaks gives the coupling constant unambiguously.

There have been two reports of the nuclear quadrupole coupling constant, one in powder at 295 K [1], another in a single crystal at 4 K [2], and a number of reports agreeing on a temperature-independent Knight shift, summarized by Dickson and Seymour [1].

This paper presents the first measurement of the temperature dependence of the nuclear quadrupole coupling constant (e^2qQ/h) and longitudinal relaxation time (T_1) for ^{25}Mg in metallic magnesium. The coupling constant determination was made by measuring the frequency separation ν_0 between the inner $(1/2, 3/2)$ and $(-1/2, -3/2)$ satellites where $\nu_0 = 3e^2qQ/20h$. The outer satellites were also observed but were

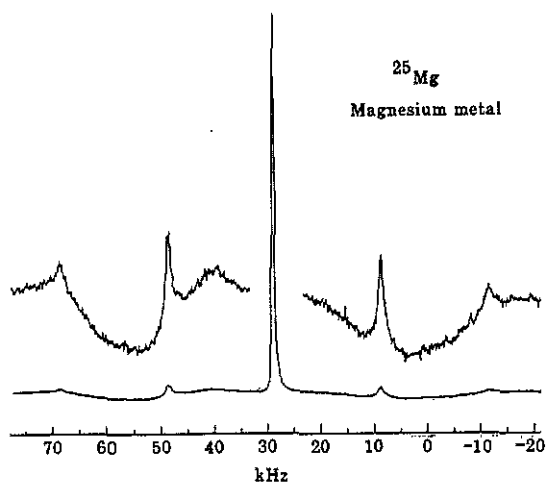


Figure 1. Powder absorption mode spectrum for ^{25}Mg ($I = 5/2$) in magnesium metal showing the central transition and the four satellites. Two sections of the trace with an expanded vertical scale are also displayed to exhibit the satellites clearly.

appreciably weaker. The relaxation study was made with the central ($1/2, -1/2$) transition. The temperature dependence of the Knight shift was also checked.

2. Experimental details

The magnesium powder sample was Labchem technical grade with 200–300 micron particle size.

NMR measurements were made at a nominal field of 9.4 T at a frequency of 24.45 MHz with a Bruker MSL 400 spectrometer at temperatures in the range 150 K to 400 K. For the satellite observations, 250 000 to 500 000 scans were accumulated using a solid echo pulse sequence with $5 \mu\text{s}$ pulses. T_1 was determined by saturation recovery at 10 delay values using true 90° pulses of $10 \mu\text{s}$ and accumulating approximately 1000 to 5000 scans. The length of the 90° pulse was due to probe loading caused by larger than optimal magnesium particle size. The Knight shift was measured with respect to a 1.5 M aqueous solution MgSO_4 . An alternative 1 M MgCl_2 (aqueous) reference solution yielded no detectable shift with respect to MgSO_4 .

The experimental data are exhibited in figures 1 to 3 and the derived results are given in the text.

3. Analysis and discussion

3.1. Quadrupole coupling constant

The previous value of $e^2qQ/h = 281(4)$ kHz at 295 K, determined from the field dependence of the width of the central transition in magnesium powder [1], is larger than the 295 K value determined here of 266(1) kHz. Using the empirical $T^{1.5}$ dependence, which describes the temperature dependence of quadrupole coupling in many metallic systems with tolerable accuracy [3], the data in figure 2 can be extrapolated to $\nu_Q = 43.6$ kHz, corresponding to $e^2qQ/h = 290.7$ kHz. This is below and outside the errors stated for the single crystal measurement at 4 K which recorded a coupling constant of 324(6) kHz

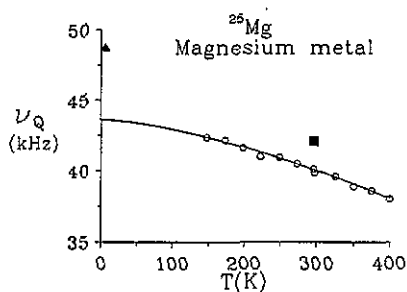


Figure 2. Temperature dependence of quadrupole frequency ν_Q for ^{25}Mg in magnesium metal. The present experimental results are shown as open circles. The full curve is the empirical expression $A - BT^{1.5}$ where $A = 43.6$ MHz and $B = 6.9 \times 10^{-4}$ MHz K $^{-1.5}$. The values from [1] (■) and [2] (▲) are also indicated.

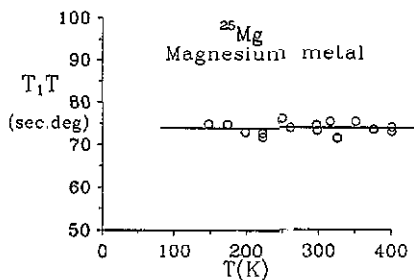


Figure 3. Temperature dependence of T_1T for ^{25}Mg in magnesium metal. The experimental results are shown as open circles and the horizontal line is the temperature-independent line of best fit.

[2]. However the general conclusion [1] that the temperature dependence is strong still holds, with an approximately 10% decrease in ν_Q between 150 K and 400 K.

With greater intrinsic precision of measurement in comparison with previous studies, a very small increase in Knight shift ($\Delta K = 330$ Hz or 13 ppm) was detected on warming from 150 K to 400 K. The Knight shift obtained at room temperature, $K = 0.1179(1)\%$, is rather higher than the previous consensus, given in [1]. Since the central transition is quite sharp (FWHM ~ 500 Hz at 9.4 T), K can be measured to good precision. Making a correction for second order quadrupole shift increases this value by only 0.7 ppm; the similar correction to the Knight shift measured at 1.4 T derived in [1] increases its value by 32 ppm to 0.115(4)%, which then agrees with the present value within the estimated error.

It is interesting to compare this result with those for the other divalent hexagonal metals, beryllium [4], cadmium [3] and zinc [3]. For beryllium (^9Be ; $I = 3/2$), a parallel study to the present one, in which the ^9Be satellite splitting was measured, indicated no detectable temperature dependence of ν_Q or Knight shift [5]; this is consistent with previous observations summarized in [3]. For cadmium (^{113}Cd ; $I = 1/2$), on warming between 150 K and 400 K, there is an approximate 15% increase in Knight shift; furthermore, γ - γ angular correlation (TDPAC) measurements using ^{111}Cd indicate a 12% decrease in ν_Q . For zinc, TDPAC measurements using ^{67}Zn indicate a 7% decrease in ν_Q over the same temperature range.

3.2. Relaxation time

While no previous values for T_1 in magnesium have been published, an estimate of 0.19 s at 295 K can be made via the Korringa relation, using the measured Knight shift and assuming free electrons [6]. An *a priori* calculation by Jena *et al* [7], based on a pseudopotential band structure, yields $T_1 = 0.20$ s at 295 K. The present measurement is $T_1 = 0.245$ s at this temperature. It can be seen from figure 3 that the product T_1T is

constant to good approximation in the temperature range 150 K to 400 K with an average value of 74(2) s K.

Acknowledgment

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