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Abstract. A high-precision observation of NMR in zinc metal at 295 K is reported. The ^{67}Zn nuclear quadrupole coupling ($C_q = e^2qQ/h$) and isotropic and axial components of the Knight shift (K_{iso} and K_{ax}) have been determined, as well as the temperature variation of C_q and K_{iso} in a 283 K range around 295 K. The large positive value for the temperature coefficient of K_{iso} is comparable to that of cadmium, and a similar explanation appears likely. At 295 K the following values are obtained: $C_q = 11.983(5)$ MHz, $K_{iso} = 1776(5)$ ppm and $K_{ax} = -124(5)$ ppm.

1. Introduction

There are a large number of scientifically and industrially important zinc products and compounds for which it would be valuable to have a characterization method, such as NMR, complementary to powder x-ray diffraction. However reports of ^{67}Zn NMR investigations of solids have been sparse. The only available stable isotope of zinc with $I > 0$, viz. ^{67}Zn, $I = 5/2$, has a natural abundance of only 4.1% and a low magnetic moment, so that, even at high magnetic fields, long signal averaging times may be required for spectra with acceptable signal to noise. Although the observation of ^{67}Zn NMR in cubic compounds, e.g. ZnS (sphaelerite), ZnSe, and ZnTe [1], presents only difficulties associated with low sensitivity and the probe ringing artefacts associated with low frequencies, the nuclear quadrupole interaction attendant on nuclear spin $I = 5/2$ presents additional linewidth problems in powder specimens of non-cubic compounds which can lead to difficulties in observation associated with short free induction decay. Nevertheless some observations, for compounds which have zinc in positions of non-cubic point symmetry, have been reported, e.g. for ZnO and ZnS (wurtzite) [1]. Since the ground state nuclear quadrupole moment for ^{67}Zn is $^{67}Q = 0.15 \times 10^{-24}$ cm^2 (comparable to those of ^{27}Al, ^{63,65}Cu and ^{69,71}Ga), the quadrupole interactions, in general, can be substantial. This is the case for ZnO, where NMR has yielded a value for the nuclear quadrupole coupling constant at room temperature of $C_q = e^2qQ/h = 2.407$ MHz, together with an accurate temperature coefficient around 293 K [1]; on heating from 250 to 400 K the value of C_q increases by 60 kHz.

In the case of zinc metal, the ^{67}Zn nuclear quadrupole interaction, e^2qQ/h, has been reported from Mössbauer [2, 3] and NQR [4] measurements, which yield a variety of coupling constants at 4.2 K, viz. 13.8(4) MHz; [2], 12.45(2) MHz [3] and 13.620(8) [4]. The first observation of ^{67}Zn NMR in zinc metal was by Abart *et al* [5] in a measurement at 4.2 K, using a field sweeping technique, which yielded a value of $C_q = 12.73(4)$ MHz. No subsequent NMR observation has been reported. A measure of the temperature dependence of the ^{67}Zn nuclear quadrupole coupling in zinc metal has been obtained from time-differential perturbed angular correlation (TDPAC) measurements [6] using an excited

state of ^{67}Zn ($I = 9/2$; 605 keV). However the use of liquid helium temperatures and exotic short-lived isotopes precludes the adoption of these techniques for general material characterization.

The observation of ^{67}Zn NMR in zinc metal by Fourier transform NMR at a fixed frequency and around 295 K is reported below. The precision in determination of edge singularities of the central $(-1/2, 1/2)$ powder lineshape, together with the sharp definition of the inner satellite transitions at 295 K, permitted an accurate determination of the isotropic Knight shift, together with the first determination of the axial component of the Knight shift. A temperature dependence for the Knight shift was also measured, for the first time, up to nearly two thirds of the melting point.

2. Experimental details

The spectra were obtained using a Bruker MSL 400 at a frequency of about 25.1 MHz in a field of 9.4 T. The material used here was standard laboratory grade and no special effort was made to obtain high purity. For example, the zinc specimen was in the form of zinc dust used as a standard catalytic material, and produced commercially by condensation of vaporized zinc. The particles were in the form of spheres with diameters ranging from the order of 20 μm to less than 1 μm No impurities, apart from oxygen, were detectable by EDAX spectroscopy. The total metal impurity level is estimated at less than 0.5%. The extremely sharp edge singularities of the ^{67}Zn lineshape are consistent with a low level of impurity.

Because of the weak signals encountered here, and the rapid decay of the free induction decay associated with the broad lines, it is essential to use an echo sequence to obtain the true time zero for the Fourier transform and efficient phase cycling to eliminate spurious signals. Furthermore it is also essential to use sufficiently short pulses to obtain a spectral power coverage to completely excite the whole broad lineshape. For example, the width of the ^{67}Zn spectrum for zinc metal at 9.4 T and 295 K is 180 kHz . For this frequency width it is essential to use pulses in the echo sequence of 4 ms duration or less. With such pulse durations it is possible to change the spectrometer frequency by amounts of 50 kHz and check that the entire $(-1/2, 1/2)$ powder lineshape moves rigidly by this offset amount. Similarly, the $\theta = 90°$ powder singularities from the inner $(1/2, 3/2)$ and $(-3/2, -1/2)$ transitions were checked by shifting the offset frequency. The spectra were obtained in a transverse solenoidal coil. The 4 μs pulse was shorter than that for a true $\pi/2$ pulse for the coil and pulse power used here.

Table 1. ^{67}Zn nuclear parameters: variation with temperature.

T (K)	K_{iso} (ppm)	K_{ax} (ppm)	C_q (MHz)
149	1706(5)	—	12.256(5)
219	1733(5)	—	12.167(5)
295	1776(5)	−124(5)	11.983(5)
371	1828(5)	—	11.742(5)
432	1896(5)	—	11.523(5)

Approximately 20 000 scans were collected for non-ambient temperatures. At 295 K, 300 000 scans were collected for the spectrum in figure 1(a). The temperature range covered is that of safe operation of the probe assembly. The NMR data derived at each temperature
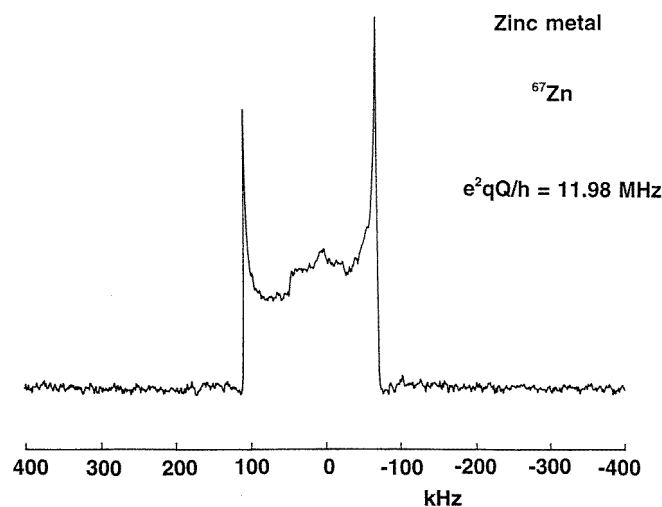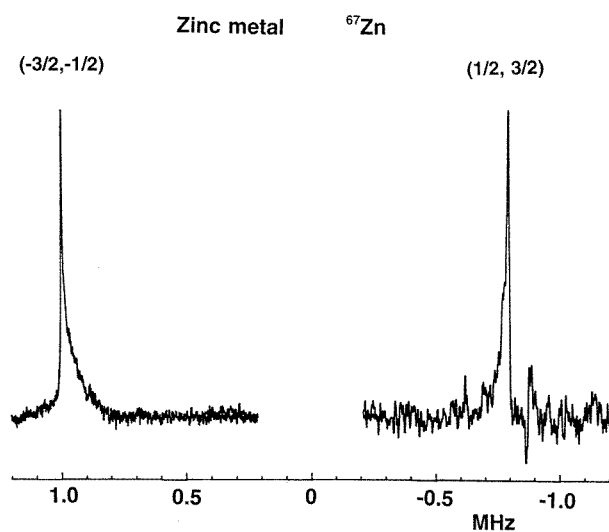
Figure 1. (a) $(-1/2, 1/2)$ and (b) $(-3/2, 1/2)$ and $(1/2, 3/2)$ ^{67}Zn NMR powder lineshapes for zinc metal at 295 K.

are given in table 1. The shift reference zero was set by the line from ZnSO4 in aqueous solution.

The powder lineshapes for the $(-1/2, 1/2)$ transition and the $(-3/2, -1/2)$ and $(1/2, 3/2)$ satellite transitions at 295 K are exhibited in figure 1. Note that because of the (uniaxial) hcp structure of zinc there will, in principal, be an axial component of the Knight shift, K_{ax}. The existence of K_{ax} must be taken into account when analysing the central $(-1/2, 1/2)$ line shape to obtain $^{67}C_q$. The correct C_q is obtained from the separation of the two inner satellite transitions shown in figure 1(b); $C_q = (20/3)\nu_q$, where ν_q is the frequency difference between these two satellites. Knowing the value of ν_q, the value of K_{ax}

can then be determined from the spacing, Δ, between the edge singularities of the central transition, together with a value for the Knight shift. The temperature dependences of both C_q and K_{iso} (figure 2) were obtained by additional measurements at two temperatures above and two below room temperature. This was considered adequate sampling since the temperature variation of both quantities was smoothly monotonic.
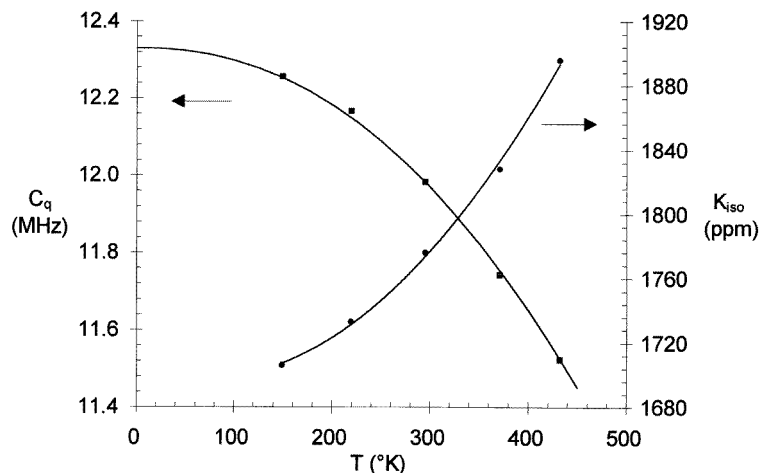

Figure 2. $C_q(T)$ and $K_{iso}(T)$ for ^{67}Zn in zinc metal. The curve through the measured points for C_q is an empirical power law fit, $A - BT^{2.2}$; the data points at 4.2 K are from the NMR results of [5] ($\square$) and the Mössbauer results of [2] ($\bigcirc$). The curve through the K_{iso} points is a guide to the eye.

The Knight shifts recorded here for metallic zinc are comparable with those observed in the β-brass system, $Cu_{1+x}Zn_{1-x}$, [7], which has the CsCl structure. The spectrum for one of these alloys is included below for comparison (figure 3(a)). Also exhibited is the spectrum for ZnO (figure 3(b)), which is likely, *a priori*, to be the main impurity in a finely powdered zinc metal specimen.

3. Discussion

Considering the method of preparation, the clean ^{67}Zn spectrum obtained here for zinc (figure 1(a)) is remarkable. It is possible that the small peak observed near zero shift is due to disordered or defective ZnO since its shift lies close to the centre of the ^{67}Zn spectrum for crystalline ZnO (figure 3(b)).

The sharpness of the peaks (singularities) in the $(-1/2, 1/2)$ spectrum for Zn metal in figure 1(a) is due to the low isotopic abundance and low value of the magnetic moment of ^{67}Zn. Since the edge singularities are so sharply defined, the temperature dependence of C_q can be measured more accurately than its absolute value, where the dipolar, or residual line broadening, has to be taken into account in the simulation of the spectrum. The peak to peak separation of the singularities is proportional to C_q^2 (in the limit of small K_{ax}), which enables the temperature dependence of C_q to be measured quite sensitively. Observation, at room temperature, of the $\theta = 90°$ powder singularities from the $(-3/2, -1/2)$ and $(1/2, 3/2)$ first-order quadrupole satellites (figure 1(b)) yielded a true value of C_q, and comparison with the value derived from the $(-1/2, 1/2)$ second-order lineshape enabled the value of
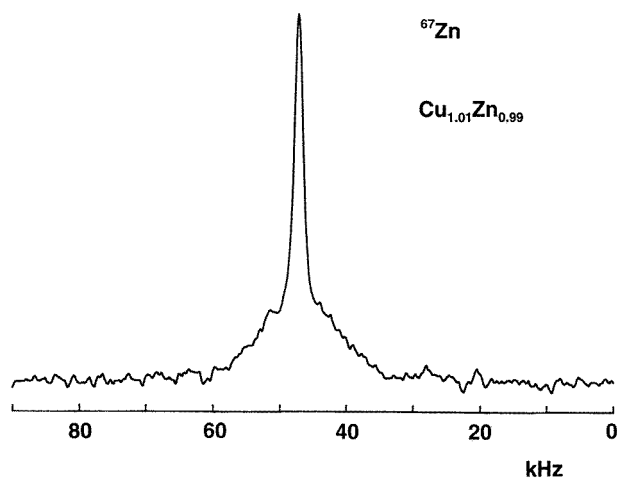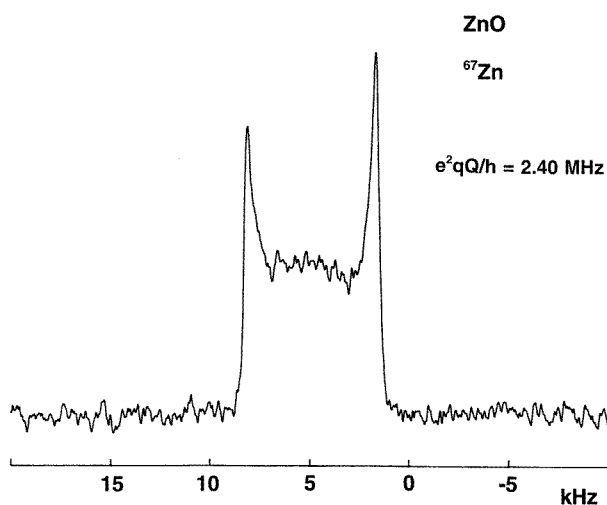
Figure 3. ^{67}Zn powder lineshapes for (a) $Cu_{1.01}Zn_{0.95}$ and (b) ZnO; $-1/2, 1/2$ transition.

K_{ax} to be determined from the following relationship (for $I = 5/2$) [8]:

$$K_{ax} = 5\nu_q[\nu_{(2)q} - \nu_q]/\nu_L^2$$

where ν_L is the Larmor frequency of ^{67}Zn. This analysis yields a value of $K_{ax} = -1.24(5) \times 10^{-4}$, which is sufficiently small that it is required only as a first-order correction term, added to the estimate $C_{(2)q}(= 20\nu_{(2)q}/3)$ from the second-order lineshape, to give the true C_q, where $C_{(2)q} = 4(2\nu_L\Delta)^{1/2}$, and Δ is the splitting between the edge singularities of the second-order $(1/2, -1/2)$ spectrum. Since the first-order satellite lineshapes were not easily measured at other than room temperature, the 296 K value of K_{ax} was used to correct $C_{(2)q}$ values at other temperatures. This procedure assumed that temperature variations in K_{ax} would contribute to C_q only to second-order in a small correction term.

The approximate (good to first-order in K_{ax}) expression

$$\nu_q = \nu_{(2)q} - K_{ax}\nu_L^2/5\nu_{(2)q}$$

was used to correct the value of $\nu_{(2)q}$ derived simply from Δ.

Note that an independent estimate of K_{ax} may be made by identifying the step feature at approximately 62 kHz shift (figure 1(a)) with the feature ν_4 (defined in [8]), and taking the shift difference $\nu_{1,4}$ between the high-frequency edge (ν_1) at 115.7 kHz and the step. The alternative expression for the axial Knight shift is then

$$K_{ax} = \nu_{1,4}/\nu_L - \nu_q^2/2\nu_L^2 = -1 \times 10^{-4}.$$

This estimate is less accurate than the former due to the difficulty of precisely defining the step. The former value is preferred here.

To compare the values of C_q derived here near room temperature with the Mössbauer, NQR and NMR results at 4.2 K, an extrapolation to low temperatures must be made. To do this, an empirical curve was fitted to the data, displayed in figure 2, using the power law form $C_q = A - BT^n$, with $n = 2.2$, which yielded the value $C_q(4\ \text{K}) = 12.334(5)$ MHz. (Note that an often used exponent $n = 1.5$ gives a less satisfactory fit.) This value is just outside the quoted error limits of the Mössbauer value of 12.45(2) MHz reported in [3], somewhat below the field swept NMR value of 12.73(4) MHz [5], but well below the earlier Mössbauer [2] and NQR [4] values quoted above. The data from [2] and [5] are also included in figure 2. A first-principles calculation of the electric field gradient in zinc has been reported [9], which yields a value for C_q (assuming $^{67}Q = 0.150 \times 10^{-24}\ \text{cm}^2$) of 13.6 MHz.

There is a marked improvement in signal to noise in the spectra obtained here by FT NMR at 9.4 T around 300 K, compared with those taken at 4.2 K at about 5 T by field sweeping and recording the spin echo profile [5]. The advantage of approximately halving the linewidth at the higher field has apparently offset the large decrease in Boltzmann factor resulting from working at the higher temperature. The central and the satellite lineshapes are considerably sharper than is suggested by the spectra given in [5], which were from specimens of high-purity, well annealed, fine powder. Note that a sharply defined $(-1/2, 1/2)$ lineshape is essential for any determination of the Knight shift since $\Delta \gg K_{iso}$.

The temperature variation of C_q for the excited nuclear state ^{67}Zn ($I = 9/2^+$; 605 keV) has been measured over the same temperature range explored here by TDPAC [6]. Within the limit of the experimental error shown in [6] the fractional variation of C_q found for this isomeric state was the same as that measured here for the ground state.

The isotropic Knight shift, K_{iso}, was derived from the data using the expression

$$K_{iso} = K_h - \nu_q^2/2\nu_L^2 - K_{ax}$$

where K_h is the shift for the high-frequency singularity of the $(-1/2, 1/2)$ lineshape. Again, for reasons outlined above, the room-temperature value of K_{ax} was used at all temperatures. Since the K_{ax} correction amounted to approximately 7% of the total shift, a variation in K_{ax} of say 10% over the temperature range investigated would contribute less than 1% to K_{iso}. The most striking features of the $K_{iso}(T)$ plot (figure 2) are (i) the magnitude of the temperature coefficient and (ii) the increase of this coefficient with temperature. Qualitatively similar behaviour for K_{iso} is observed for ^{113}Cd in cadmium [10]. Indeed, this should not be unexpected since the two metals have strong structural and electronic similarities. An explanation of the large positive temperature coefficient for K_{iso} in cadmium has been given [11] in which 'lattice vibrations effectively decrease the strength of the lattice potential and make it more isotropic. As the temperature increases the energy bands become

more free-electron-like and the s-character of the wave functions on portions of the Fermi surface increases', thus increasing K_{iso}. In the absence of a detailed calculation it seems likely that a similar explanation applies for zinc. It is noted however, in passing, that the temperature dependence of K_{iso} for ^{25}Mg in metallic magnesium (also hcp) is much gentler right up to the melting point at 923 K, with $^{25}K_{iso}(923$ K$) - ^{25}K_{iso}(293$ K$) \approx 40$ ppm [7].

Finally it may be noted that ^{67}Zn Knight shifts of the same order as for zinc metal are observed in β-brass, $Cu_{1+x}Zn_{1-x}$. As an example, the lineshape for a β-brass with 49.5 at.% Zn is displayed in figure 3(a). The Knight shift for this alloy is 1879 ppm at room temperature. Further NMR investigation of the CuZn system has revealed the presence of defect structure in the ^{67}Zn (and also ^{63}Cu) lineshape for these alloys and demonstrated the sensitivity of the ^{67}Zn Knight shift to relatively small variations in stoichiometry [7].

In conclusion it is emphasized that, for NMR material characterization, the low sensitivity of detection for ^{67}Zn is often offset by the sharpness of the resonance. Furthermore, since Δ is inversely proportional to the magnetic field, the magnitude of C_q in many non-cubic zinc-containing materials is such that, at fields of order 10 T, the $(-1/2, 1/2)$ lineshape may be adequately excited by single-frequency pulsed FT NMR without the need for frequency stepping or field sweeping techniques.

Acknowledgments

References

[1] Bastow T J and Stuart S N 1988 *Phys. Status Solidi* b **145** 719
[2] Vetterling W T and Pound R V 1977 *Workshop on New Directions in Mössbauer Spectroscopy (Argonne, 1977)* ed G J Perlow; *AIP Conf. Proc.* **38** 27
[3] Steiner M, Potzel W, Karzel H, Schiessl W, Kofferlein M, Kalvius G M and Blaha P 1996 *J. Phys.: Condens. Matter* **8** 3581
      See also Potzel W, Forster A and Kalvius G M 1978 *Phys. Lett.* **67A** 421
[4] Kaufman E N, Brookeman J R, Canepa P C, Scott T A, Rasmussen D H and Perepezko J H 1979 *Solid State Commun.* **29** 375
[5] Abart J, Pelangie E, Socher W and Voitlander J 1983 *J. Chem. Phys.* **78** 5468
[6] Christiansen J, Heubes P, Keitel R, Klinger W, Loeffler W, Sandner W and Witthuhn W 1976 *Z. Phys.* B **24** 117
[7] Bastow T J and West G W, unpublished data
[8] Baugher J F, Taylor P C, Oja T and Bray P J 1969 *J. Chem. Phys.* **50** 4914
[9] Blaha P, Schwartz K and Dederichs P H 1988 *Phys. Rev.* B **37** 2792
[10] See the summary in Carter G C, Bennett L H and Kahan D J 1977 *Metallic Shifts in NMR* Part I (Oxford: Pergamon) and references therein
[11] Kasowski R V and Falicov L M 1969 *Phys. Rev. Lett.* **22** 1001