Knight shift in liquid zinc and its temperature dependence

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Measurements of the temperature dependence of the Knight shift of ^{67}Zn in liquid zinc metal have been carried out in the range of 685–1000 K in an external magnetic field of about 38 kG. The magnetogyric ratio of ^{67}Zn has also been measured in the reference compound $ZnCl_2$.

The study of nuclear magnetic resonance in metals has generally increased the understanding of the character of the conduction electrons at the Fermi surface. The NMR properties are strongly affected by the magnetic fields produced by the magnetization of the conduction electrons. In this context the Knight shift, the spin-lattice relaxation time, and the internuclear interactions such as the indirect spin-spin and spin-dipolar interactions are of particular significance. The goal of the experiment reported here was the determination of the Knight shift and its temperature dependence in metallic zinc.

Using a high-field and high-temperature NMR spectrometer developed by Ploumbidis[1,2] we measured the magnitude, sign, and temperature dependence of the Knight shift of ^{67}Zn in liquid zinc metal. The experimental temperature dependence of the Knight shift K is shown in Fig. 1.

The positive shift of ^{67}Zn in liquid zinc at 692.7 K was found to be $K(^{67}\mathrm{Zn}) = (0.3368 \pm 0.0004)\%$. The temperature coefficient of K for the linear part of the function $K(T)$ was found to be $A = 2.7 \times 10^{-5}\% K^{-1}$. Values of K for zinc at the melting point calculated by Heighway and Seymour[3] were found to be 0.52% and 0.47%. We could not observe any NMR signal of ^{67}Zn in the solid zinc metal (powdered sample) over a temperature range of 295–692 K. We suppose this is mainly due to the quadrupolar splitting in the noncubic (hexagonal) crystalline structure of the solid zinc.

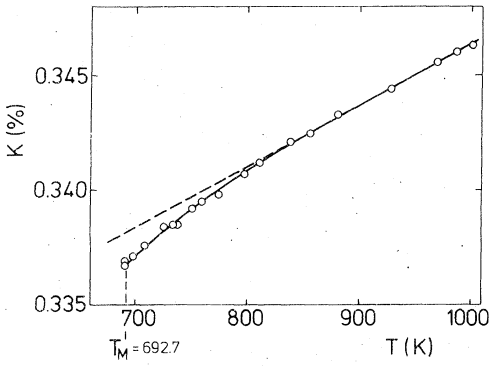

FIG. 1. Experimental Knight shift K for ^{67}Zn in liquid zinc as a function of temperature. In the supercooled state the NMR signal could be observed only down to 10 K below the melting point.

The metal sample used in this experiment was prepared from bulk material with a purity of 99.999% supplied by Materials Research Corp., New York. It was crushed and sieved to obtain particle sizes in the range of 50—100 μm. The crushed metal was then mixed with the threefold amount of Al_2O_3 powder to insure that most of the metal particles were insulated from each other. The ^{67}Zn NMR was observed in a field of 38.775 kG produced by a superconducting solenoid, and at a resonance frequency of 10.366 MHz produced by a modified Pound-Knight-Watkins NMR detector. Using a PAR lock-in amplifier with a 100-sec time constant we achieved a signal-to-noise ratio of about 25 at a temperature of 700 K. The NMR signal of ^{67}Zn in liquid zinc is shown in Fig. 2.

The reference compound was a 5-molar $ZnCl_2$ aqueous solution. For ^{67}Zn we found a magnetogyric ratio $\gamma/2\pi = 0.266\,419 \pm 0.000\,003$ kHz/G. The following other values for this ratio are given in the literature: 0.266 28 kHz/G by Weaver[4]; 0.266 386 kHz/G by Epperlein *et al.*[5], 0.2664 kHz/G in Varian NMR data tables. In our NMR experiment we controlled the magnetic field[6] by means of deuterium NMR with an error of 100 mG for a field of 38.775 kG, and the resonance frequency counter by means of a frequency calibration standard with an error of 5 Hz for a frequency of 10.366 MHz. For the determination of the Knight shift of ^{67}Zn in liquid zinc metal we

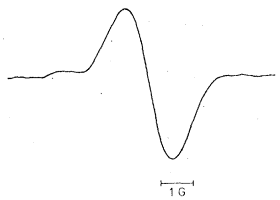

FIG. 2. NMR signal of ^{67}Zn in liquid zinc at 700 K (derivative of the absorption curve).

used the value of the magnetogyric ratio of ^{67}Zn in $ZnCl_2$ resulting from our experiment. No diamagnetic corrections were made in obtaining this value.

To our knowledge no NMR data for zinc in zinc metal in both solid and liquid state have been reported up to this date.[7] Magnetic susceptibility data are also rare for zinc metal in the liquid state. The temperature dependence of the magnetic susceptibility in liquid zinc for the relatively small range of 693—823 K has been given by Wachtel and Übelacker.[8]

It is known that under definite conditions the temperature-dependent Knight shift and susceptibility of a number of transition metals can be analyzed into their different contributions (i.e., spin and orbital contributions) by means of the Knight shift K versus susceptibility χ diagram introduced by Clogston *et al.*[9] The efficiency of the K-vs-χ analysis has recently been shown once more by the NMR study of molybdenum metal[10] in which the orbital part of K and χ is dominant. For an analysis in the above sense for liquid zinc one needs more extensive experimental data related directly or indirectly to the electronic properties of liquid zinc metal. In the near future we expect to obtain more NMR and susceptibility data concerning zinc metal so that there will be a basis for such an analysis of its electronic structure. This view is supported by a recent publication by Das and Misra[11] in which the orbital, spin, and spin-orbit contributions to the magnetic susceptibility of zinc metal have been calculated.

ACKNOWLEDGMENT

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