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NMR CURIE-LAW THERMOMETRY FOR SOLID HYDROGEN*

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An estimate is presented for the temperature difference between a sample of solid hydrogen and its container, based on the known thermal boundary resistance and the heat load due to ortho-para conversion. NMR Curie-Law thermometry is used to measure the true temperature of hydrogen cooled by a dilution refrigerator.

Recently, there has been considerable interest in the solid-state phase transitions exhibited by solid hydrogen, particularly for temperatures < 300mK (for a review, see reference 1). The purpose of this article is to point out the difficulty of performing accurate thermometry on hydrogen at these temperatures, and to describe a method for dealing with this problem.

The molar ortho-concentration X of solid hydrogen decays according to the rate law

$$dX/dt = (-0.019/hr)X^2 \qquad (1)$$

resulting in a release of heat

$$dQ/dt = 3.1\times10^3 erg/(sec\ cm^3)VX^2. \qquad (2)$$

where V is the sample volume. Most low temperature experiments are designed to make external heat leaks much smaller than this. Thus a sample of solid hydrogen can induce large temperature differentials (e.g. between a sample chamber and a thermometer affixed to the mixing chamber of a dilution refrigerator), which are not present for samples of other types.

The thermal boundary resistance between the hydrogen and the sample chamber presents a more difficult problem. Reynolds and Anderson[2] measured the boundary resistance Z_B between hydrogen and copper for $1K \lesssim T < 7K$. As expected, they found that Z_BT^3 was a slowly varying function of temperature. At 1K they observe

$$Z_BT^3 = 3\times10^{-6} cm^2K^4sec/erg \qquad (3)$$

When this is substituted into the functional form suggested by the acoustic-mismatch theory of boundary resistance,[2] the following expression is obtained for the heat flow between sample and sample chamber:

$$dQ/dt = A(T_s^4-T_c^4)\ x \qquad (4)$$
$$8.33\times10^4\ erg/(sec\ cm^2K^4)$$

Here T_s is the sample temperature, T_c is the sample chamber temperature, and A is the area of the boundary between them.

Fig. 1 shows a sample chamber developed for NMR studies on solid hydrogen in a field of 7T. The chamber itself is a toroidal inductor, which in combination with an outer capacitive section forms a UHF resonant circuit. To provide thermal contact between the chamber and the hydrogen sample, 12,000 teflon-insulated copper wires, 0.1mm in diameter, are soldered to the floor of the chamber. The total surface area is $240cm^2$ per cm^3 of free volume. Based on eqn.(4) the minimum sample temperature achievable (as $T_c \to 0$) for ortho concentration X is then

$$T_{min} = (112mK)X^{1/2} \qquad (5)$$

Even for X as small as 0.2, this predicts a minimum achievable sample temperature of 50mK.

These results suggest that the temperature of the hydrogen sample be measured directly, rather than relying on the temperature of the sample chamber. This may be done by measuring the area of the NMR absorption line, which varies as 1/T according to Curie's law. This is feasible with hydrogen because of the short spin-lattice relaxation times ($T_1 \sim$ 20ms at 300mK, for X=0.3.)[3] In our experiments, the

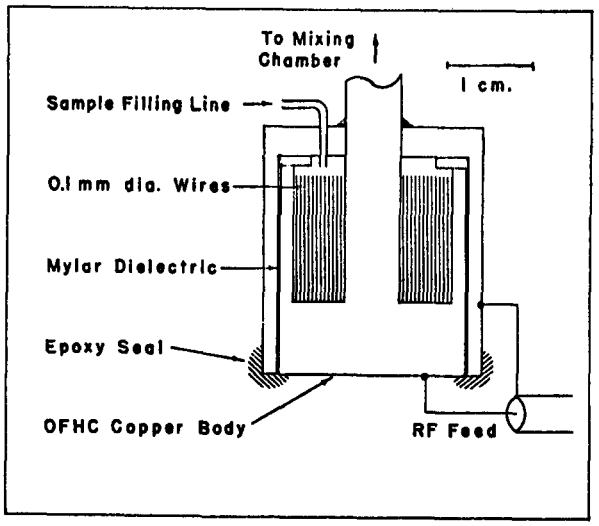

Figure 1. Sample chamber for solid hydrogen NMR measurements at 300 MHz.

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derivative of the NMR line (obtained by lock-in detection) is digitized and integrated twice by a microcomputer. In order to assure linearity of the frequency scale, the computer is also part of a feedback loop involving an electronic counter which scans the frequency through the NMR line. A carbon resistance thermometer is used for interpolation, and also for temperature stabilization.

In order to apply Curie's law, it is necessary to have one or more reliable temperature reference points. If these use measurements of the sample chamber temperature, then they must be at sufficiently high temperature for the differential temperature calculated from eqn.(4) to be small. One convenient reference temperature, of course, is 4.2K but its use presents two problems: 1) The temperature is an order of magnitude larger than those used in these studies and the resulting small line areas are subject to larger fractional errors. 2) The sensitivity of the NMR system is proportional to the Q of the resonant cavity, which in turn depends on the conductivity of copper at the measurement temperature. Experimentally the electrical characteristics of the cavity change slightly between 4K and 1K.

For these reasons, we have chosen to use the superconducting transition temperatures of Zn (851mK) and Cd (519mK) as our fixed points. The transitions are observed through changes in the mutual inductance of coils surrounding samples of the two materials.[4] The fixed points were used to calibrate the carbon resistance thermometer (a Speer grade 1002, 1/2 watt, 220 ohm resistor) in zero magnetic field. The magnetoresistance of this type of resistor has been measured by Sample, et. al. in fields up to 14T.[5] This allows us to transfer the zero-field calibration to fields in which NMR thermometry is possible.

The NMR system response must be carefully adjusted in order to achieve consistent line areas. Our numerical integration routine chooses a derivative zero so as to make the total integral of the derivative line zero. No other baseline corrections are applied. With this integration algorithm we have found it possible to adjust the NMR system for absence of dispersion signal and simultaneously for flat frequency response. Our procedure consists in adjusting the tuning of the UHF NMR bridge, and the frequency response of the RF amplifiers in order to make the baselines flat both in a direct oscilloscope display of the NMR line, and in the integrated derivative NMR line. (The lock-in output is a derivative with respect to magnetic field, and is insensitive to slopes in the frequency response curve.)

Figure 2 presents typical results comparing temperatures computed on the basis of lineshape areas with the resistance of the carbon resistor. Plots are shown for two values of X and

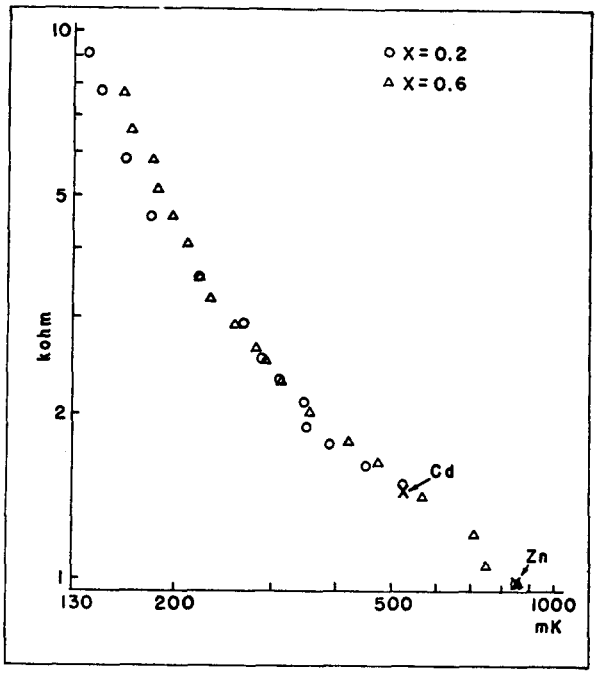

Figure 2. Resistance of a carbon thermometer vs. hydrogen sample temperature, for two ortho-concentrations X. The sample temperature is measured by NMR thermometry. The superconducting transitions of cadmium and zinc are indicated.

they clearly demonstrate the effects of ortho-para conversion heating at the lower temperatures. The apparent values of T_{min} are consistent in magnitude with eqn.(5). (The teflon insulation on the thermal contact wires probably affects the value of Z_B.) In the absence of a hydrogen sample, the ultimate temperature of this refrigerator was measured with a $Ni(Mn^{54})$ nuclear orientation thermometer[6]. The same carbon resistor used for making the measurements in Fig. 2 indicated a resistance of 30kohm at 30mK. An extrapolation of the curves in Fig. 2 would imply a considerably higher temperature for this resistance, again in agreement with the behavior predicted by eqn.(4).

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