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High-pressure–low-temperature apparatus for NMR study of phase transitions

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An apparatus has been developed for nuclear-magnetic-resonance (NMR) measurement of relaxation times in solids at hydrostatic pressures to 7 kbar and temperatures down to 77 K. Sample temperature can be controlled accurately with ±2 mK stability allowing measurement of dynamic phenomena very near phase transitions. The high-pressure vessel is equipped with additional electrical feedthroughs so that dielectric measurements can be carried out concurrently, providing additional information on ferroelectric phase transitions.

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INTRODUCTION

In this paper we describe a high-pressure vessel and cryostat system designed for nuclear-magnetic-resonance measurements of dynamic phenomena near the ferroelectric phase transition in solids of the KH_2PO_4 family. The transition temperatures of these crystals vary as a function of applied pressure, and spin lattice relaxation times can be as long as many minutes, so the system must control sample temperature and pressure with a high degree of stability and accuracy. For the materials of interest the apparatus requirements are: (1) maintain temperatures from 100 to 240 K with 2 mK stability, (2) maintain hydrostatic pressures as high as 5 kbar using He gas as a pressure medium, and (3) provide electrical access to the sample space for NMR and dielectric measurements under these conditions. A number of high-pressure NMR experiments have been reported which are reviewed by Benedek[1] and more recently by Jonas,[2] and Jonas *et al.*[3] None of the techniques described in the literature fulfill both the temperature and pressure range requirements stated above and thus were not readily adaptable to our purposes. Designs of pressure vessels usable to 4 kbar and above, which are cooled by flowing gas systems over the range from room temperature to 77 K, have been reported,[4–6] but the temperature stability of these systems is at best about ±50 mK. The system we have built uses a liquid nitrogen Dewar and nested isothermal shields for temperature control and a beryllium–copper pressure vessel usable to 7 kbar. We first describe the mechanical details of the pressure vessel and cryostat, followed by an explanation of the temperature control system. Next the design and construction of high-pressure electrical feedthroughs is discussed. Last, we present features of the NMR sample coil and associated circuitry as well as some properties of the arrangement for making dielectric measurements.

I. APPARATUS DESCRIPTION

A cross-sectional view of the pressure vessel and the bottom end of the cryostat is shown in Fig. 1. The high-pressure vessel (A) has a sample space 28.7 mm in diameter by 40.6 mm long and is supported by 6.35-mm-o.d. × 1.59-mm-i.d. high-pressure tubing (B) supplied by American Instrument Co.[7] The pressure seal between tubing and pressure vessel is made with a gland nut and collar (C) of 304 stainless steel. The pressure vessel is surrounded by a copper isothermal shield (D) suspended from the pressure tubing by means of a clamp. This shield is, in turn, surrounded by a second isothermal shield (E) maintained at liquid-nitrogen temperature by contact with a liquid-nitrogen reservoir (F). The space inside the cryostat wall (G) is evacuated to 10^{-5} Torr to minimize heat conduction to the sample vessel. To prevent fluctuations in pressure caused by varying levels of liquid nitrogen in the reservoir the pressure tubing is isolated by a vacuum space (H) and thermally grounded to the reservoir bottom by a copper clamp (I).

Temperatures within the system are monitored by copper–constantan thermocouples (J1–J3) mounted at the top of the inner shield, and at the top and bottom of the pressure vessel. The temperature of the pressure vessel is also monitored by CS-400 capacitance sensors (K1, K2) made by Lake Shore Cryotronics[8] which are placed in cavities at the top and bottom of the vessel. Sample cell temperature is controlled by a heater (L) which is powered by a Lake Shore Cryotronics Model CSC-400 capacitance temperature controller.[8] The temperature of the inner shield is maintained by a heater (M) which compensates for the heat lost to the liquid-nitrogen reservoir through a thermal leak (N) and to a lesser extent through leads, pressure tubing, and radiative cooling. The thermal leak consists of several strands of copper braid connected between the nitrogen reservoir and shield. Increasing the cross section of the thermal leak decreases the thermal time constant but increases the rate of liquid nitrogen consumption. The shield heater is supplied by a home built power supply which controls the heater voltage so that the difference between thermocouples (J1) and (J2) is 1 ± 0.1 K. Thus, as the pressure vessel temperature is varied under the control of the CSC-400, the inner shield temperature is automatically held 1 K colder than that of the pressure vessel.

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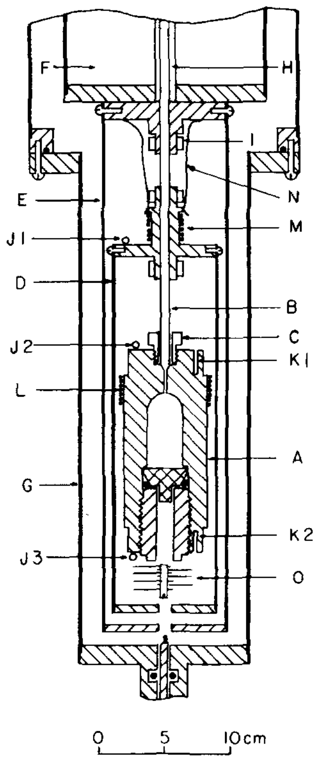

FIG. 1. High-pressure vessel and bottom section of low-temperature cryostat system.

The pressure vessel heater is made by winding a layer of number 28 copper wire around the vessel, cementing it in place with varnish, winding another layer in the opposite direction, cementing it in place, and continuing until the coil resistance is about 10 Ω. The completed coil is coated with varnish and wrapped with alternating layers of Teflon tape and aluminum foil. The inner shield heater is constructed in a similar manner using number 28 nichrome wire. Electrical connections from thermocouples, temperature sensors, and heaters are routed through the top of each isothermal shield and along the outside surface of the liquid-nitrogen reservoir to vacuum feedthroughs at the top of the cryostat. To minimize thermal gradients, all of the leads are thermally grounded with varnish and copper brackets at each point of temperature control, namely at the top of the pressure vessel, the top of the inner isothermal shield, and at the bottom of the liquid-nitrogen reservoir.

Access to the sample space of the pressure vessel is by means of a conventional unsupported area-type seal shown in Fig. 2. The seal consists of a mushroom plug (A), a deformable Be–Cu O ring (B), and a support plug (C). The three high-pressure electrical feedthroughs required are spaced 120° apart in the mushroom plug. The pressure vessel, mushroom plug, support plug, and O ring were machined from ½ hard Berylco 25 Be–Cu rod stock supplied by Cabot Berylco.[9] Before machining, the Be–Cu rods were ultrasonically tested for internal flaws by United States Testing Co.[10] After machining, all points of contact between the various components were carefully polished on a lathe using 1-μm alumina grit. With the exception of the O-ring seal, the Be–Cu components were hardened for 3 h at 315 °C in an argon atmosphere.

The electrical feedthroughs use a spherical geometry and pressure seals of extrudable plastic similar to those described by Vassiliou and Jamieson.[11] However, feedthroughs for NMR experiments must be nonmagnetic and have as high a conductivity as possible. For this reason the design was modified so that the feedthroughs could be fabricated from Be–Cu and hardened. The feedthroughs consist of a plug (D) 4.76 mm in diameter with a hemispherical end which rests in a matching depression 1.43 mm deep in the mushroom plug. The feedthrough plug is electrically isolated from the mushroom plug by a Teflon disc 1.8 mm thick (E) which makes the pressure seal by extruding around a brass pin 1.27 mm in diameter (F) threaded into the feedthrough plug. External electrical connections are made to these pins which pass through holes in the mushroom plug. The holes in the mushroom plug are 1.52 mm in diameter for the first 2.5 mm to limit the amount of Teflon extruded around the brass pins. For the remaining distance the holes are 2.29 mm in diameter to provide clearance for insulating sleeves 2.03 mm in diameter (G). The plugs are held in place by alignment pins which pass through a pressure plate (H) and are isolated from it by Teflon sleeves (I).

The feedthrough plugs are machined to have 4.76-mm-diam hemispheres at one end which are drilled and tapped in the center for the brass pins. The hemispheres are then polished with 1-μm alumina grit on a polishing cloth. The matching depressions are made with a 4.76-mm ball end mill and are polished with alumina grit using a fixture made by welding a 4.76-mm-diam ball bearing to a drill rod. The Teflon seal is preformed by pressing 4.76-mm ball bearings into the Teflon disk using the depressions in the mushroom plug as a form. After the depressions have been made in the disk the ball bearings are clamped in place with the pressure plate and holes are drilled for the brass rods using the holes in the mushroom plug as a guide. When the feedthroughs are assembled the screw

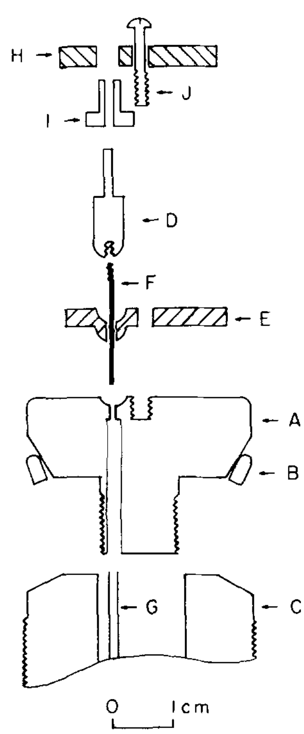

FIG. 2. High-pressure vessel unsupported area seal (A–C) and exploded view of one high-pressure electrical feedthrough (D–J).

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(J) is tightened to about 2 N-m torque so that the plugs compress the Teflon gasket enough to seal at low pressure.

The NMR sample coil is a cylindrical coil of number 28 copper wire 8 mm in diameter by 20 mm long mounted in the sample space of the pressure vessel. One end of the coil is grounded and the other is connected via one of the above-described high-pressure feedthroughs to a variable capacitor (O) mounted at the bottom of the vessel. The capacitor is placed inside the vacuum system near the sample coil to minimize the resistance of this series resonant circuit and maximize its Q. Resonance is achieved by adjusting the variable capacitor with a retractable rotary motion feedthrough mounted in the bottom of the cryostat vacuum can. Following Clark and McNeil,[12] the transmit and receive functions are separated at the other end of this capacitor, where the rf pulses are supplied through a coaxial cable and the pulse response is routed to the receiver by a second cable. Both coaxial cables are Type UT-47 50 Ω microcoax made by Uniform Tubes.[13] They are routed to the top of the cryostat in the same way as the other leads, where they connect to triaxial cables from our NMR spectrometer.

Measurement of the dielectric constant of KH_2PO_4-type crystals requires electrodes on the crystal faces perpendicular to the ferroelectric c axis. Electrodes are made by vacuum sputtering a layer of gold approximately 20 nm thick onto faces which have been prepared by polishing with successively finer grades of alumina grit (63, 8, and 5 μm). Leads of number 30 copper wire are attached to each electrode with a spot of silver epoxy[14] and the leads are soldered to the alignment pins of the high-pressure feedthrough plugs. For KH_2PO_4-type crystals dielectric measurements are usually carried out on samples in the shape of thin plates with the large faces perpendicular to the crystal c axis. For our NMR measurements larger crystals with the longest dimension along the c axis are desirable. While the NMR samples are not of optimum geometry for accurate dielectric measurements, it is possible to determine directly how near the sample is to the ferroelectric transition.

The system described has been used for proton spin-lattice relaxation time measurements on KH_2PO_4 in the range from 155 to 125 K with a temperature stability of ±2 mK and at pressures to 3.5 kbar. This apparatus was built for use with a Varian V-3800 electromagnet having a 12.7-cm air gap, but the design could be adapted to other magnet configurations so long as the working volume is not prohibitively small.

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