Reprinted from:

THE REVIEW OF SCIENTIFIC INSTRUMENTS VOLUME 43, NUMBER 11 NOVEMBER 1972

High Pressure ENDOR Cavity*

W. T. Doyle, T. F. Dutton, and A. B. Wolbarst†

Department of Physics, Dartmouth College, Hanover, New Hampshire

(Received 6 April 1972; and in final form, 26 June 1972)

The apparatus employed in a room temperature examination of the effects of intense hydrostatic compression (to 11½ kilobars) upon F center hyperfine interactions is described.

Several workers have performed EPR and NMR at high pressures,[1] but the necessity of bringing both microwave and rf power into a pressure chamber presents unique difficulties. The first high pressure ENDOR (electron nuclear double resonance) measurements were made by H. P. Liu,[2] whose apparatus[3] could function to 2½ kilobars.

The design reported here was used in an ENDOR study of F centers in alkali halides and hydrides at pressures to 11½ kilobars.[4,5] The new system represents a simplification and strengthening of the previous model and consists of three distinct components[6]: the beryllium–copper bomb itself, A(1,2); the X-band microwave input and cavity unit, B(1,2), which slides into the bomb from above and is secured by a large retaining nut, D(2); and an rf and compression fluid feed assembly, C(1,2), which attaches to the pressure vessel from below. Contact between the rf input lead in C and the ENDOR coil E(1) in B is made within the bomb by means of male, H(1), and female I(1) Sub-Minax[7] couplings.

I. THE PRESSURE VESSEL, A(1,2)

The outer diameter of the pressure vessel is determined by the magnet pole face separation. For greater strength, however, the dimensions of the cavity within can be reduced. There is currently under construction a K-band unit designed to withstand 20 kilobars, the pressure region of the polymorphic phase transitions in the potassium halides.

Four vessels, designed to withstand 10 kilobars, have been constructed; the first three of these failed at 11½, 8, and 7 kilobars, respectively. In vessel 1, a corkscrew fracture followed the internal threading (which secures the retaining nut, D) through a 360° twist and snapped the cylinder in half. Subsequent bombs were given shallower and round (rather than V shaped) threading. After lines of stress were noted at the interior base of the exploded vessels 2 and 3, the bottom of the ENDOR coil support, F(1), and the high pressure chamber itself were given a large radius rounding. Figure 1 indicates the corrected design; previously (Fig. 2), these two parts had been cylindrical rather than hemispherical. Vessel 4 was also given a rounded O-ring seating and a polished interior surface. This last bomb has held reliably to 8½ kilobars, the maximum value of pressure chosen for our present work.

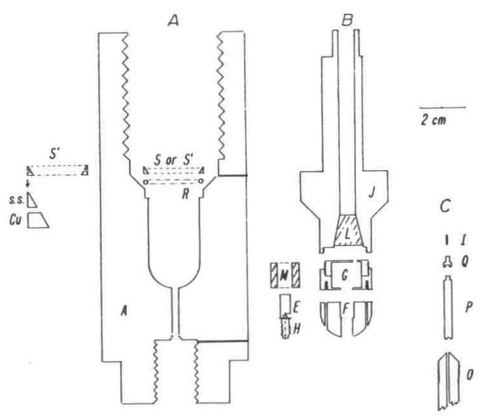

Fig. 1. Schematic of high pressure cavity and vessel.

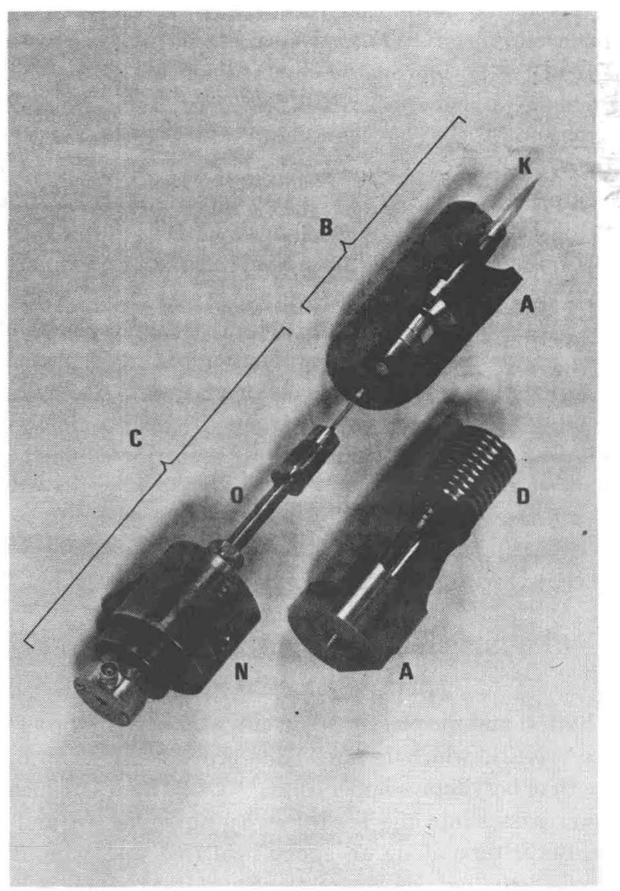

Fig. 2. Exploded view of cavity, vessel, and Tee.

All four bombs were machined from full work hardened (temper H) 6.35 cm BeCu bar stock. It is likely that the reliability of the pressure vessels is strongly dependent upon the post machining precipitation hardening process.[8] The first bomb was aged for approximately 3 h at 370°C. The second and third were held at 315°C for 3 h, resulting in maximum tensile strength and hardness. The fourth was taken to 290°C for 1 h. It is felt that this last aging procedure gives a good compromise between ductility and tensile strength.

II. ENDOR CAVITY ASSEMBLY, B (FIGS. 1, 2)

Microwave radiation passes down a tapered section of X-band waveguide, maintained above cutoff by a Lucalox[9] rod, K(2). The microwaves travel along the rod and through a Lucalox pressure window, L(1), [which is premanently pressed into its support J(1) to provide the high pressure seal], and into the cylindrical cavity G(1) via an eccentric coupling hole. (Lucalox is an extremely hard ceramic made by G.E., with dielectric constant of 9.9, and loss tangent of 2.5×10^{-5}). The cavity, resonant in the TE_{011} mode at approximately 9.2 GHz, contains a thick-walled Lucalox tube, M(1); the advantages of this arrangement are discussed in Ref. 3. The coil support, F(1), is held to the bottom of the cavity by brass screws; the single loop rf coil, E(1), projects up through a large central hole in the bottom of the cavity. One side of the coil is grounded, and the other is attached to the terminal of a male Sub-Minax connector, H(1), whose connecting end passes down through the bottom of F(1). A groove across the upper face of F(1) retains a flat strip of Teflon upon which the sample crystal sits, and several narrow diameter holes facilitate the flow of pressure fluid to and from the cavity.

A great convenience of the present system is the ability to optimize the degree of coupling by rotating the section of tapered waveguide (above B) relative to the cavity, thereby altering the relationship between microwave polarization and the position of the eccentric coupling hole. One can achieve the same effect by unscrewing the entire cavity away from the pressure window by part of a turn, such that the cavity's coupling hole is more (or less) concentric with the Lucalox window.

III. PRESSURE FLUID AND rf POWER FEED THROUGH, C(1,2)

Both rf and the pressure fluid enter the system through a Tee,[10] N(2), which is suspended beneath the bomb by a length of beryllium–copper tubing,[11] O(2). Radio frequency power passes into the Tee through a pipestone seal and up the BeCu tube along an epoxy insulated #28 wire. The female coupling element of the Sub-Minax, I(1), is held rigidly 2.5 cm beyond the end of the BeCu tube by a narrow hollow stem of Kel-F, P(1), tipped with a Teflon nipple Q(1).

A tapered BeCu electrode, which seats in the pipestone cone to form the electrically conducting high pressure seal in the Tee, is silver soldered to the #28 wire. Soft solder appears to work harden with compression, leaving a mechanically and electrically poor joint, and indium solder is not mechanically strong enough to withstand inadvertent tugs on the #28 wire. Indium solder is used at other high pressure electrical junctions, where mechanical strength is not of such crucial importance.

The unsupported area seals in the manganin wire high pressure gauge (which is not shown in Fig. 1 or 2), the Tee, and the bomb are of conventional design. The Buna-N synthetic rubber O-rings, R(1), and 303 stainless steel backup rings, S(1), seldom need to be replaced, even after disassembling the apparatus. The scratching of backup ring seatings can be decreased by giving both rings and seatings a high polish. Dulling the leading edge of a backup ring (which initially is triangular in cross section) reduces wear on the O-ring. An alternative backup ring system, S′(1) consisting of an upper seal of 303 s.s. and a supporting washer of F.M. copper, forms a more reliable initial seal. Both pieces of S′(1), however, must be replaced after every run.

The high pressure gauge consists of a matched pair of loosely wound coils of manganin wire of known $(\partial R/R\partial P)_T$. The two (one of which is encased in a separate high pressure chamber and reached via a pipestone seal electrode) form part of an ac null detecting bridge circuit and give rise to an estimated error of less than 1%; agreement with a Bourdon tube gauge is consistently better than 3% at pressures to $2\frac{1}{2}$ kilobars.

High pressures are achieved by means of a hybrid combination of two pumps designed by Daniels.[12] A 1:1:1 mixture of Dial-AX,[13] kerosene, and pentane is found to be suitable pressure conducting fluid.

ACKNOWLEDGMENTS

The authors would like to acknowledge the valuable assistance of Raymond V. Duquette and Percival B. Woods, instrument makers in the Apparatus Shop at Dartmouth College.

* Research supported by a grant from the National Science Foundation.

† Current address, Department of Physics, University of Witwatersrand, Johannesburg, South Africa.

[1] H. G. Drickamer, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1965), Vol. 17.

[2] H. P. Liu, M.A. thesis (Dartmouth College, Hanover, N. H., 1968).

[3] W. T. Doyle, T. F. Dutton, and H. P. Liu, Rev. Sci. Instrum. **40**, 171 (1969).

[4] A. B. Wolbarst, "Pressure Dependence of *F* Center Hyperfine Interactions," to be published, J. Phys. Chem. Solids **33** (1972).